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New air-stable zinc complexes formed from cyanoacrylate- and methylenemalonate-based $[N_2O_2]$-ligands and their role as catalysts in epoxide–CO_2 coupling†

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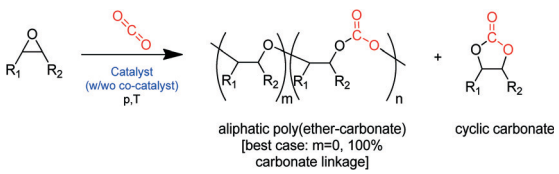
The synthesis of a range of zinc complexes based on ligands displaying an N_2O_2-framework with cyanoacrylate and/or malonate functionality is presented. Some complexes could be examined *via* X-ray diffraction on single crystals, giving interesting insights into the structures of these zinc compounds, some of them building coordination polymers. The zinc complexes are highly active in the catalytic conversion of propylene oxide with CO_2 to afford propylene carbonate. The study of this class of complexes leads to reactivity trends showing that ligands with aromatic diamino linkers and malonate fragments display the highest catalytic activity under mild conditions.

Introduction

During the last two decades, the catalytic formation of aliphatic polycarbonates (aPC) and cyclic carbonates (CC) from CO_2 and epoxides has been a growing area, attracting increasingly the focus of both academia and industry.[1] This is partly due to the fact that using an epoxide, an intrinsic reactive substrate, and having on the other hand a limited number of final products can possibly provide a rich chemistry and good outcomes in a short period of time. Both organic carbonates, CC and aPC, (Scheme 1) are actually useful products found in some industrial applications: the monomers, for example, are used as polar, non-toxic solvents or electrolytes in lithium ion cells,[2] whereas the copolymers find applications as complements to the more common aromatic polycarbonates and as starting materials for specialty materials (*e.g.* PPC as sacrificial binders in the ceramic industry a.k.a. "evaporative casting patterns"[3] or as telechelic polymers in the formation of "environmentally friendly" polyurethanes[4]).

An increasing number of catalytic systems, homogeneous as well as heterogeneous, have been reported for the coupling of epoxides with CO_2 in the literature. Fig. 1 undeniably shows this trend as well as the related number of publications and reviews released.

Although the "market" seems to be saturated with promising catalytic systems, there is still a big demand for cheap and environmentally friendly systems. To have a chance to compete with the known systems, a "good" catalyst should display a highly versatile and rather straightforward synthesis (the lower the number of synthetic/purification steps the better it is), should be highly selective and, considering the rising energy costs, should be also active under mild conditions.[5] We have already reported the successful use of iron and aluminium



Scheme 1 Possible products of the reaction of carbon dioxide with epoxides.

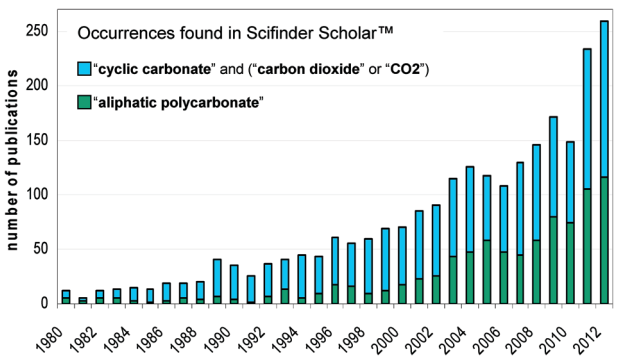


Fig. 1 Publication trend dealing with organic carbonates from CO_2 and epoxides.

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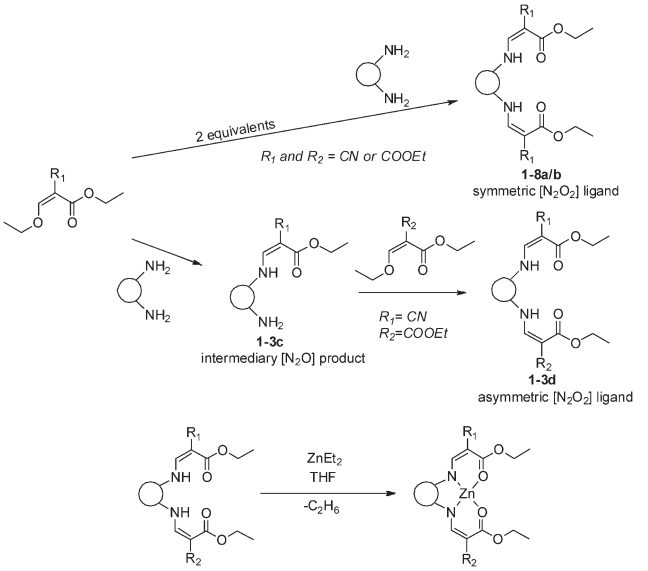
complexes in the coupling of CO_2 with epoxides, the catalysts involving simple N_2O_2-ligands displaying cyanoacrylate and malonate functionalities.[6,7] Considering the preponderant role of some zinc catalysts in the formation of organic carbonates and especially polycarbonates,[8] we concentrated afterwards on the related N_2O_2–zinc complexes and could isolate a new, easy-to-handle Zn–N_2O_2 complex that is revealed to be highly active in the coupling of CO_2 and epoxides.[9] We report here on the related zinc-derivatives presenting N_2O_2 ligand systems with aminoacrylate and/or aminomalonate moieties in the backbone as well as different diamino-linkers, with a.o. substituted 1,2-phenylenediamine linkers. Among the 19 zinc complexes, it was possible to structurally characterize five of them *via* X-ray diffraction on single crystals. This range of zinc complexes was particularly tested in the coupling of CO_2 with PO to evaluate the influence of the ligand structure on the catalytic activity and connect the results to the first Zn-complex of this row.[9] Most of the complexes were revealed to be highly active in the formation of PC, in some cases, under mild reaction conditions.

Results and discussion

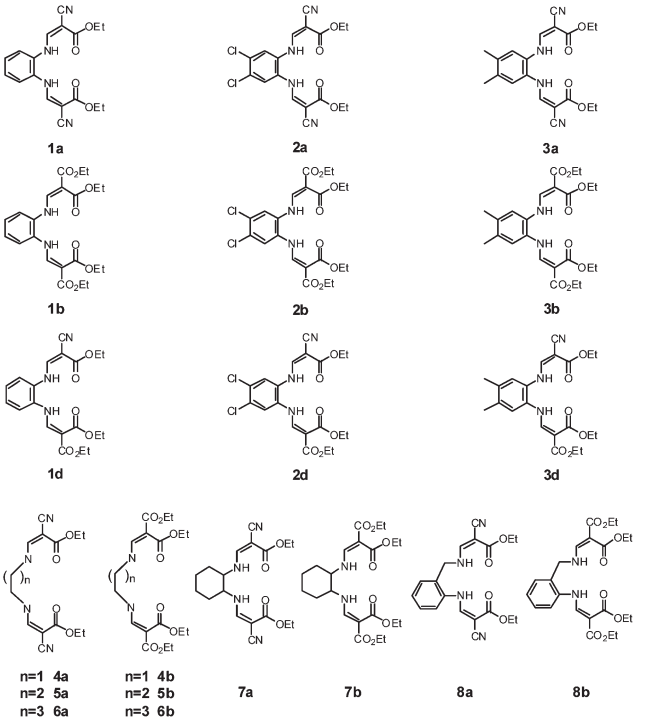
Synthesis

The N_2O_2-chelating ligands used to form the catalysts are known since the 1940s,[10] obtained from the reaction of a diamine linker with diethyl ethoxymethylenemalonate or ethyl 2-cyano-3-ethoxyacrylate under liberation of ethanol. These two starting compounds are commercially available and relatively cheap esters principally obtained *via* the reaction of triethyl orthoformate with the related esters.[11]

This class of ligands was thoroughly studied by the group of E.-G. Jäger[12] and B. Weber[13] as interesting model complexes of specific enzymes or as building blocks of larger systems with promising magnetic properties. The synthesis of the symmetrically substituted ligands (R_1=R_2=CN or CO_2Et) is straightforward, giving the ligands in high yields (Scheme 2). The asymmetrically substituted ligands are obtained in a two-step procedure with isolation of a "mono-substituted" N_2O-ligand that further reacts with a second ester to give the sought after asymmetric ligand. These N_2O-ligands have actually also great potential and their complexes will be reported elsewhere. The reaction works particularly well with 1,2-phenylenediamine linkers whereas only a small range of non-aromatic diamine-linkers leads to N_2O_2-ligands in reasonable yields (Scheme 3 for overview). Further reaction of the ligands with organometallic zinc precursors is undemanding and realized in anhydrous tetrahydrofuran as the solvent (Scheme 2). Once the ligand was dissolved in the solvent, diethyl zinc dissolved in hexane was added drop-wise to yield under liberation of ethane the zinc complex almost quantitatively. Interestingly, the solubility of the complexes based on ligands with nitrile moieties is lower than that of the related malonato derivatives, with the formation of nitrile-bridged structures (*vide infra*) being apparently responsible for the easy and rapid separation of the complexes from the reaction mixture.



Scheme 2 General synthetic ways to the iminoacrylate and amidomalonate ligands and formation of the zinc complexes.



Scheme 3 N_2O_2 ligands used in this study and their nomenclature; for the zinc complexes' nomenclature: Zn[ligand number], *e.g.* Zn[**8b**].

Crystallography

Single crystals suitable for crystal structure analysis could be only isolated with complexes based on symmetric ligands: nitrilo Zn[**1a**] (see ref. 9), Zn[**2a**] and Zn[**3a**] and malonato ligands Zn[**1b**], Zn[**2b**] and Zn[**3b**]. Crystallization was performed using concentrated DMSO solutions to yield after

a couple of days at room temperature well-formed yellowish rhombuses (crystallographic data of the structures have been deposited at the Cambridge Crystallographic Database Centre; supplementary publication no. CCDC complex Zn[**2a**]: 974320, Zn[**3a**]: 974319, Zn[**1b**]: 974318, Zn[**2b**]: 974321 and Zn[**3b**]: 974322). Structural investigation revealed clearly two different types of structure: on the one hand, the malonate-based ligands yielded monomeric structures with zinc being either pentacoordinated (tetragonal pyramidal with H_2O or DMSO as the apical neutral ligand) or hexacoordinated (distorted octahedral geometry with two axial DMSO). On the other hand, the cyanoacrylate-based ligands led to coordination polymers comparable to "metal–organic frameworks" displaying zinc atoms octahedrally coordinated with the nitrile groups of one ligand coordinating to the next neighbouring zinc complex, occupying the next axial position. A similar behaviour has been reported for related iminoacrylate zinc complexes by M. Kröger *et al.*[14] The alternating coordination pattern leads to characteristic zig-zag chains propagating along the *b* axis (Fig. 2). In both types of zinc complexes, the N_2O_2-ligands occupy the equatorial plane. Complexes Zn[**2a**] and Zn[**3a**] are isostructural displaying the same zig-zag chain patterns; for the sake of brevity only the structure of Zn[**2a**] will be discussed in detail. The zinc atoms are slightly distorted from the ideal geometry with a maximal distortion from the mean N_2O_2-plane of 0.019 Å (0.024 Å for complex Zn[**3a**]), with the N_2O_2-ligand being almost planar as found in the related iron and zinc–N_2O_2 complexes.[6,9] Crystal data and structure refinement details can be found in Table 1 while selected bond lengths and angles for complexes Zn[**2a**] and Zn[**3a**] are listed in Table 2. The bond lengths found within the N_2O_2-coordination sphere of Zn[**2a**] display a perceptible asymmetry probably due to the influence of the intramolecularly coordinated nitrile group. Hence, the Zn–O and Zn–N bonds are a tad longer on the side bearing the coordinating nitrile: Zn(1)–N(3) with 2.0600(10) Å and Zn(1)–O(3) with 2.1127(9) Å, whereas the other side shows 2.0579(9) Å and 2.0692(10) Å for Zn(1)–N(1) and Zn(1)–O(1), respectively. The Zn–O_{DMSO} bond is, with Zn(1)–O(5) of 2.1709(9) Å, significantly longer than that found in the related DMSO-tetragonal pyramidal zinc-"salen" complexes and a tad shorter than that found in the relatively scarce hexacoordinated zinc salen DMSO educts like the salphen complex reported by A.W. Kleij and co-workers which displays Zn–O_{DMSO} distances ranging from 2.217 to 2.263 Å.[15] The intramolecular Zn(1)–N(4) bond length is 2.1990(9) Å, being notably longer than other intermolecular Zn–nitrile bonds as *e.g.* reported by Kröger *et al.* (Zn–O: 2.040(9) Å).[14] Interestingly, the bonding of the nitrilo groups to the zinc center has no influence on the length of the C–N triple bond. The four (N,O)–Zn angles measured within the plane showed "well balanced" features, with angle O(1)–Zn–O(3) being the widest with 98.66(3)° while angle N(1)–Zn–N(3) is the smallest with 80.93(4)°. The

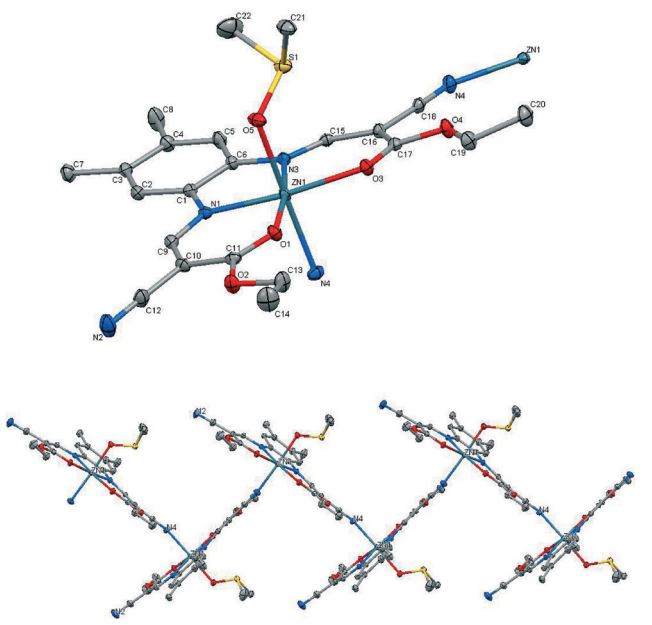


Fig. 2 Displacement ellipsoid plot of Zn[**3a**] $\{[Zn(\mathbf{3a})(DMSO)]\}_\infty$ showing the polymeric structure.

Table 1 Crystal data and structure refinement details of complexes Zn[**2a**] and Zn[**3a**] (more detail in Experimental)

Crystal data	Zn[**2a**] $\{[Zn(\mathbf{2a})(DMSO)]\}_\infty$	Zn[**3a**] $\{[Zn(\mathbf{3a})(DMSO)]\}_\infty$
Empirical formula	$C_{20}H_{20}Cl_2N_4O_5SZn$	$C_{22}H_{26}N_4O_5SZn$
Molecular mass	564.73	523.90
Crystal color	Yellowish	Yellowish
Crystal size (mm^3)	0.122 × 0.052 × 0.029	0.144 × 0.092 × 0.064
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c* (no. 14)
a (Å)	1092.76(6)	10.7526(5)
b (Å)	1174.95(6)	11.5952(5)
c (Å)	1815.19(10)	19.6353(9)
α (°)	90	90
β (°)	97.7840(10)	100.7200(10)
γ (°)	90	90
V ($Å^3$)	2309.1(2)	2405.38(19)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.624	1.447

Table 2 Selected bond lengths (Å) and angles (°) of complexes Zn[**2a**] and Zn[**3a**]

Complex Zn[**2a**]/bonds–angles		Complex Zn[**3a**]/bonds–angles	
Zn(1)–N(1)	2.0600(10)	Zn(1)–N(1)	2.0944(18)
Zn(1)–N(3)	2.0692(10)	Zn(1)–N(2)	2.0519(17)
Zn(1)–O(1)	2.0579(9)	Zn(1)–O(1)	2.0764(15)
Zn(1)–O(3)	2.1127(9)	Zn(1)–O(3)	2.0880(15)
Zn(1)–O(5)	2.1709(9)	Zn(1)–O(5)	2.1658(15)
Zn(1)–N(4)	2.1990(9)	Zn(1)–N(3)	2.2133(18)
C(12)–N(2)	1.151(9)	C(10)–N(3)	1.149(9)
C(18)–N(4)	1.151(9)	C(16)–N(4)	1.154(9)
N(1)–Zn(1)–N(3)	80.93(4)	N(1)–Zn(1)–N(2)	80.42(7)
N(3)–Zn(1)–O(3)	89.34(4)	N(2)–Zn(1)–O(3)	90.10(6)
N(1)–Zn(1)–O(1)	91.07(4)	N(1)–Zn(1)–O(1)	88.96(6)
N(4)–Zn(1)–O(5)	174.49(4)	N(3)–Zn(1)–O(5)	169.96(7)
O(1)–Zn(1)–O(3)	98.66(3)	O(1)–Zn(1)–O(3)	100.56(6)
N(1)–Zn(1)–N(4)	92.52(4)	N(1)–Zn(1)–N(3)	97.88(7)
N(1)–Zn(1)–O(5)	89.95(4)	N(1)–Zn(1)–O(5)	91.55(6)
O(3)–Zn(1)–O(5)	88.53(4)	O(3)–Zn(1)–O(5)	85.37(6)

angle involving zinc, DMSO and coordinated nitrile is 174.49(4)°.

In contrast, the presence in the malonate-based ligands **1b**, **2b** and **3b** of an ester group hinders the formation of polymeric structures in the complexes and leads to typical monomeric structures for the zinc compounds Zn[**1b**], Zn[**2b**] and Zn[**3b**], with DMSO or water occupying the remaining coordination site(s). The coordination geometry is either pentacoordinated (tetragonal pyramidal with H_2O or DMSO as the apical neutral ligand) as found in related zinc salen complexes[16] or, more uncommon, hexacoordinated, with a distorted octahedral geometry and two axial DMSO.[15] Considering the tetragonal pyramidal aqua complex Zn[**1b**] (Fig. 3), the bond lengths found within the N_2O_2-coordination sphere are within a small range for both independent molecules. Crystal data and structure refinement details can be found in Table 5 while selected bond lengths and angles of complex Zn[**1b**] can be found in Table 3. The shorter Zn–O bond is Zn(2)–O(16) with 1.998(19) Å involving a coordinated water molecule and is one of the shortest measured in related zinc-"salen/salphen" aqua complexes. This can be tentatively explained by the presence of an extended hydrogen bond network. This network involves the coordinated water molecule of one complex and the non-coordinated ester groups of two neighbouring complexes as indicated by the distances O(14)–O(9): 2.658 Å, O(9)–O(10): 2.676 Å and O(1)–O(18):2.642 Å and O(18)–O(5): 2.654 Å. This contributes to some extent to the commonly found alternating "tête-bêche" arrangement of the complex in the crystal.[17]

In the related tetragonal pyramidal DMSO complex Zn[**2b**] (Fig. 4), the bond lengths found within the N_2O_2-coordination sphere are within a small range displaying a well balanced structure as reported in many cases with discrete N_2O_2–metal complexes. The shorter bond is Zn(1)–O(9) with 2.0082(11) Å involving a strongly coordinated DMSO molecule.

In the case of the octahedrally coordinated complex Zn[**3b**] (Fig. 5), the structure is slightly distorted from an ideal octahedron, with a maximal distortion from the mean N_2O_2-plane of 0.109 Å (plane N1, O5, N2, O1), with the N_2O_2-ligand being almost planar and occupying the equatorial positions as expected. The ligand is, in that particular case, more bent than in the tetragonal pyramidal complexes. One of the two apical DMSO molecules is disordered and displays a longer Zn–O bond with 2.247(3) Å whereas the opposite bond length is 2.121(3) Å. These distances are typical for hexacoordinated N_2O_2–zinc complexes with DMSO in apical positions.[15] The O(9)–Zn(1)–O(10) angle demonstrates, with 161.19°, higher distortion of the octahedral coordination compared to the coordination geometries found in the

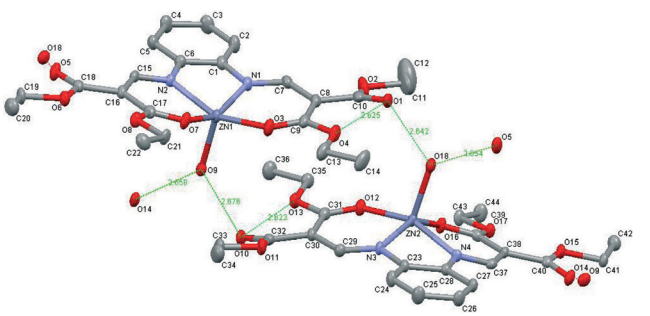


Fig. 3 Displacement ellipsoid plot of Zn[**1b**] [Zn(**1b**)$(H_2O)]_2$ showing the two independent molecules.

Table 3 Selected bond lengths (Å) and angles (°) of complex Zn[**1b**]

Bond lengths		Angles	
Zn(1)–N(1)	2.022(2)	N(1)–Zn(1)–N(2)	81.38(9)
Zn(2)–N(3)	2.024(2)	N(3)–Zn(2)–N(4)	81.49(9)
Zn(1)–N(2)	2.029(2)	N(1)–Zn(1)–O(3)	88.28(9)
Zn(2)–N(4)	2.031(2)	N(3)–Zn(2)–O(12)	88.53(9)
Zn(1)–O(3)	2.020(2)	N(2)–Zn(1)–O(7)	87.60(8)
Zn(2)–O(12)	2.023(2)	N(4)–Zn(2)–O(16)	87.51(8)
Zn(1)–O(7)	2.017(2)	O(3)–Zn(1)–O(7)	90.95(8)
Zn(2)–O(16)	1.998(19)	O(12)–Zn(2)–O(16)	89.69(8)
Zn(1)–O(9)	2.026(2)	N(2)–Zn(1)–O(9)	99.54(9)
Zn(2)–O(18)	2.020(2)	N(1)–Zn(1)–O(9)	106.19(9)
		O(7)–Zn(1)–O(9)	101.49(9)
		O(3)–Zn(1)–O(9)	105.12(9)

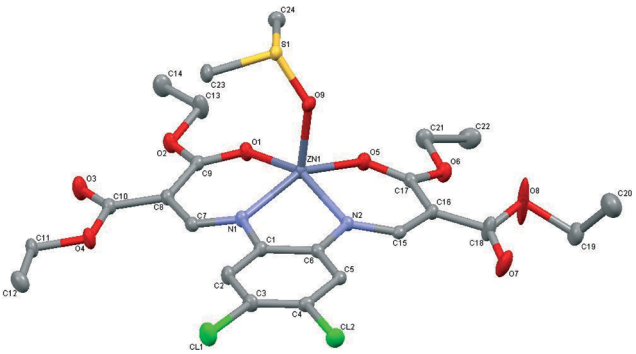


Fig. 4 Displacement ellipsoid plot of Zn[**2b**] [Zn(**2b**)(DMSO)].

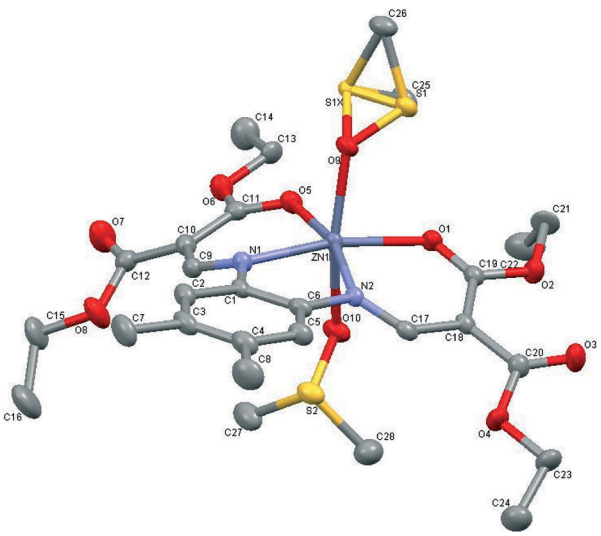


Fig. 5 Displacement ellipsoid plot of Zn[**3b**] [Zn(**3b**)$(DMSO)_2$].

coordination polymers Zn[**2a**] and Zn[**3a**] (O–Zn–N angles: 174.49(4) and 169.96(7)). Crystal data and structure refinement details of complexes Zn[**2b**] and Zn[**3b**] can be found in Table 5 while selected bond lengths and angles of both complexes can be found in Table 4. Interestingly, the comparison of the various intramolecular bonds in complexes Zn[**2a**–**3a**], Zn[**1b**–**3b**] and the related Zn–salphen–DMSO complexes reported by A. W. Kleij *et al.*[15,16,18] shows that our complexes are on the whole comparable to salphens (general trend: shorter Zn–O and a tad longer Zn–N distances for the Zn–salphens).

Catalytic tests

In order to evaluate the performance of various zinc complexes in carbon dioxide/epoxide coupling reactions, we performed catalytic screening using propylene oxide as the test substrate to obtain the related propylene carbonate, varying some reaction conditions like temperature (*T*), pressure (*p*) and catalyst concentration (*c*(cat)). For the catalytic screening, a test bench with eight 70 ml autoclaves ("IKFT-made", Stainless Steel 316Ti) equipped with magnetic stirrer, external heater and *p*,*T*-acquisition *via* PCs was applied.

Table 4 Selected bond lengths (Å) and angles (°) of complexes Zn[**2b**] and Zn[**3b**]

Zn[**2b**]		Zn[**3b**]	
Zn(1)–N(1)	2.0386(12)	Zn(1)–N(1)	2.057(4))
Zn(1)–N(2)	2.0389(12)	Zn(1)–N(2)	2.081(4)
Zn(1)–O(1)	2.0419(11)	Zn(1)–O(1)	2.064(3)
Zn(1)–O(5)	2.0279(11)	Zn(1)–O(5)	2.077(3)
Zn(1)–O(9)	2.0082(11)	Zn(1)–O(9)	2.121(3)
N(1)–Zn(1)–N(2)	80.60(5)	Zn(1)–O(10)	2.247(3)
N(2)–Zn(1)–O(5)	87.50(5)	N(1)–Zn(1)–N(2)	79.89(14)
N(1)–Zn(1)–O(1)	86.59(5)	O(9)–Zn(1)–O(10)	161.19(4)
O(1)–Zn(1)–O(5)	92.44(4)	O(5)–Zn(1)–O(1)	106.69(13)
N(1)–Zn(1)–O(9)	109.83(5)	N(1)–Zn(1)–O(5)	86.70(14)
N(2)–Zn(1)–O(9)	100.54(5)	O(1)–Zn(1)–N(2)	86.09(13)
O(5)–Zn(1)–O(9)	99.64(4)	O(9)–Zn(1)–O(5)	85.69(13)
O(1)–Zn(1)–O(9)	105.16(4)	O(9)–Zn(1)–O(1)	84.71(13)

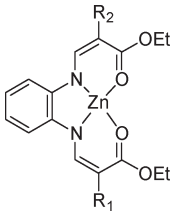
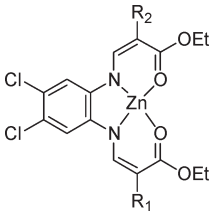
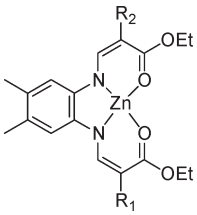
Some significant reactivity trends could be observed while running these catalytic screening tests with the 19 zinc complexes (Tables 6 & 7). The presence of a cocatalyst is necessary as it is commonly the case for most of the related catalytic systems.[19] The use of ionic tetrabutyl ammonium salts, especially Bu_4NI, is very successful due to the high nucleophilicity of the anion, whereas the use of DMAP und 1-methyl imidazole delivered the cyclic carbonate in very low yields. Both catalyst types, with either nitriles or ester groups, display high catalytic activity in the coupling reaction of PO with CO_2, delivering selectively propylene carbonate. Modifying the catalyst & cocatalyst concentrations confirmed that the catalysts are highly active: it is necessary to drastically lower the catalyst-to-substrate ratio to differentiate the catalysts and evaluate the influence of the diamino-linker (*e.g.* role of the ancillary CN and COOEt groups) and the effect of the substituents of the aromatic linkers on the reactivity. At a catalyst-to-epoxide ratio as low as 1 to 10 000 (0.01 mol%), a cyclic carbonate yield of 77% could be still reached with the malonato derivatives (entry 8 and 9, cat. Zn[**1b**], Zn[**1d**]).

The catalysts having an aromatic diamine-*ortho*-phenylene linker and ancillary ethyl ester groups present reactivity slightly higher than the ones with nitriles (Table 6, entries 8, 9 & 14, 15, ligands **1b**–**3b** & **1d**–**3d**). Interestingly, the catalysts with an aromatic, non-conjugated spacer (Table 7, ligand **8a**), in contrast to the basic *ortho*-phenylene diamino linkers, display generally lower catalytic activity. Within this class of complexes, however, the nitrile-bearing ligands have a slightly higher reactivity than the ester-bearing ones (Table 7, entries 5, 7, ligand **8a**). This trend was also apparent upon changing to pure aliphatic linkers: the catalytic activity of the related zinc complexes was definitely lower, requiring the use of higher pressure and temperature to be competitive (Table 7, comparison: entries 3, 4 *vs.* 5, 6 & 7, 8). The carbonate yields were a tad better with the nitrile-containing ligands (Table 7, entries 3, 5, 7, ligands **4a**–**6a**). This suggests that in our case an efficient N_2O_2 catalyst needs a conjugated aromatic linker and, as a corollary, good co-planarity of the metal and the

Table 5 Crystal data and structure refinement details of complexes Zn[**1b**], Zn[**2b**] and Zn[**3b**]

Crystal data	Zn[**1b**]:[Zn(**1b**)$(H_2O)]_2$	Zn[**2b**]:[Zn(**2b**)(DMSO)]	Zn[**3b**]:[Zn(**3b**)$(DMSO)_2$]
Empirical formula	$C_{44}H_{56}N_4O_{18}Zn_2$	$C_{24}H_{30}Cl_2N_2O_9SZn$	$C_{28}H_{42}N_2O_{10}S_2Zn$
Molecular mass	1059.66	658.83	696.12
Crystal color	Yellowish	Yellowish	Yellowish
Crystal size (mm^3)	0.075 × 0.057 × 0.028	0.297 × 0.247 × 0.207	0.131 × 0.056 × 0.053
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*
a (Å)	15.8662(12)	1333.44(8)	7.8991(5)
b (Å)	13.3414(11)	914.75(6)	26.6878(18)
c (Å)	23.2173(18)	2418.87(15)	15.6509(11)
α (°)	90	90	90
β (°)	96.3740(10)	103.9830(10)	97.0720(10)
γ (°)	90	90	90
V ($Å^3$)	4884.2(7)	4884.2(7)	3274.3(4)
Z	4	4	4
$D_{calc.}$ (g cm^{-3})	1.441	1.528	1.412

Table 6 Catalytic screening using PO and zinc complexes with aromatic diamine

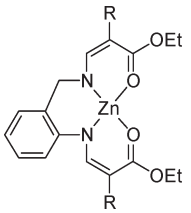
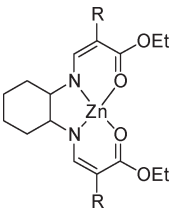
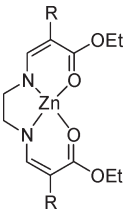
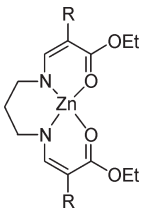
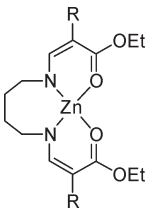
Entry	*p* (bar)	*T* (°C)	*c*(cat) (mol%)	R_1/ ligand	R_2/ ligand	Cat.	Yield (%)	TON	Cat.	Yield (%)	TON	Cat.	Yield (%)	TON
1	50	80	0.20	CN	CN	Zn[**1a**]	99	495	Zn[**2a**]	98	490	Zn[**3a**]	95	475
2				COOEt	COOEt	Zn[**1b**]	99	495	Zn[**2b**]	98	490	Zn[**3b**]	99	495
3				CN	COOEt	Zn[**1d**]	99	495	Zn[**2d**]	[a]		Zn[**3d**]	[a]	
4	50	80	0.10	CN	CN	Zn[**1a**]	97	970	Zn[**2a**]	100	1000	Zn[**3a**]	87	870
5				COOEt	COOEt	Zn[**1b**]	>99	990	Zn[**2b**]	100	1000	Zn[**3b**]	95	950
6				CN	COOEt	Zn[**1d**]	99	990	Zn[**2d**]	100	1000	Zn[**3d**]	98	980
7	50	80	0.01	CN	CN	Zn[**1a**]	64	6400	Zn[**2a**]	63	6300	Zn[**3a**]	64	6400
8				COOEt	COOEt	Zn[**1b**]	77	7700	Zn[**2b**]	75	7500	Zn[**3b**]	73	7300
9				CN	COOEt	Zn[**1d**]	77	7700	Zn[**2d**]	46	4600	Zn[**3d**]	51	5100
10	50	40	0.10	CN	CN	Zn[**1a**]	79	790	Zn[**2a**]	48	480	Zn[**3a**]	64	640
11				COOEt	COOEt	Zn[**1b**]	69	690	Zn[**2b**]	71	710	Zn[**3b**]	81	810
12				CN	COOEt	Zn[**1d**]	79	790	Zn[**2d**]	51	510	Zn[**3d**]	78	780
13	2	40	0.20	CN	CN	Zn[**1a**]	88	440	Zn[**2a**]	[a]		Zn[**3a**]	[a]	
14				COOEt	COOEt	Zn[**1b**]	93	465	Zn[**2b**]	97	485	Zn[**3b**]	92	460
15				CN	COOEt	Zn[**1d**]	90	450	Zn[**2d**]	68	340	Zn[3d]	91	455

Reaction conditions: cocatalyst Bu_4NI, *c*(cat) = *c*(cocat.), *t* = 20 h, the epoxide is the solvent. [a] Not tested because the conversion under more "friendly" reaction conditions was too low.

ligand. Considering the results of crystal structure determination of Zn[**2a–3a**] and Zn[**1b–3b**] (see above) and representing both mesomeric forms of one typical complex, it is easy to draw a parallel to the zinc salphen structure reported in the literature (Scheme 4).[15,16,18] The important role of planar, delocalized ligand architectures has been well documented in this kind of chemistry in the case of *e.g.* metalloporphyrins,[20] aluminum phthalocyanines[21] and, more directly, with related aluminum[22] and nickel[23] "salophens" (other name for salphens).

Logically, a nitrile group in such complexes should, *via* an electron withdrawing effect, enhance even more the catalytic activity of the zinc complexes. On the other hand, the formation of coordination polymers and the competition of nitrile/epoxide at the coordination center of the zinc complexes seem to go against this trend. Supporting this, in the case of ligands exhibiting a nonconjugated linker, the nitrile groups have again a positive influence on the reactivity of the zinc complexes, with the nitrile playing its role as a withdrawing group, enhancing thus the Lewis acidity of the metal center

Table 7 Catalytic screening using PO and Zn complexes with nonconjugated and aliphatic diamine linkers

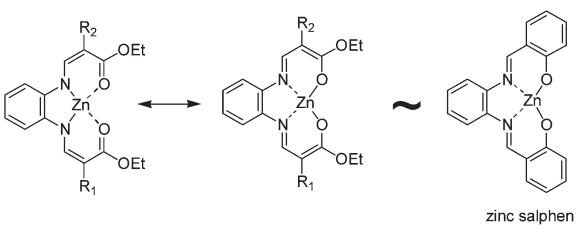






Entry	*T* (°C)	*c*(cat) (mol%)	R	Cat.	Yield (%)	Cat.	Yield (%)	Cat.	Yield (%)	Cat.	Yield (%)	Cat.	Yield (%)
1	80	0.20	CN	Zn[**8a**]	99	Zn[**7a**]	[a]	Zn[**4a**]	97	Zn[**5a**]	99	Zn[**6a**]	98
2			COOEt	Zn[**8b**]	99	Zn[**7b**]	[a]	Zn[**4b**]	92	Zn[**5b**]	99	Zn[**6b**]	80
3	80	0.10	CN	Zn[**8a**]	90	Zn[**7a**]	95	Zn[**4a**]	96	Zn[**5a**]	96	Zn[**6a**]	61
4			COOEt	Zn[**8b**]	98	Zn[**7b**]	97	Zn[**4b**]	77	Zn[**5b**]	48	Zn[**6b**]	37
5	80	0.01	CN	Zn[**8a**]	45	Zn[**7a**]	11	Zn[**4a**]	13	Zn[**5a**]	25	Zn[**6a**]	[a]
6			COOEt	Zn[**8b**]	19	Zn[**7b**]	4	Zn[**4b**]	7	Zn[**5b**]	[a]	Zn[**6b**]	[a]
7	40	0.10	CN	Zn[**8a**]	79	Zn[**7a**]	9	Zn[**4a**]	37	Zn[**5a**]	25	Zn[**6a**]	[a]
8			COOEt	Zn[**8b**]	6	Zn[**7b**]	19	Zn[**4b**]	17	Zn[**5b**]	[a]	Zn[**6b**]	[a]

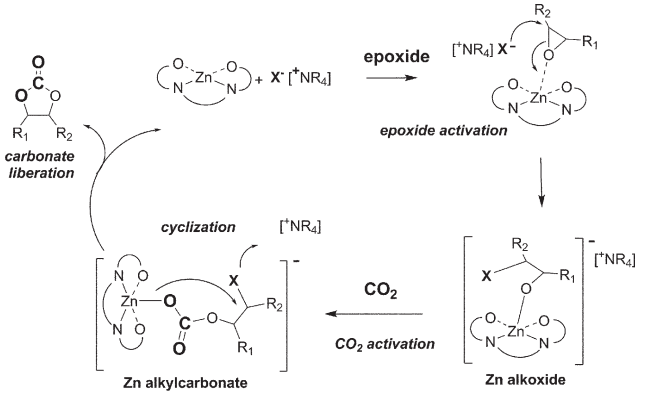
Reaction conditions: cocatalyst Bu_4NI, *c*(cat) = *c*(cocat.), *t* = 20 h, the epoxide is the solvent. [a] Not tested because the conversion under more "friendly" reaction conditions was too low.

(Table 7, entries 3, 4 with ligands **4–6a** & **4b–6b** or entries 5, 6 with ligands **8a–7a** & **8b–7b**). The formation of coordination polymers, albeit not as stable as in the case of compounds with aromatic linkers, cannot be completely ruled out. The IR spectra of Zn[**5a**] and Zn[**7a**] for instance display a weak splitting of the *ν*CN band whereas the IR spectra of Zn[**4a**], Zn[**6a**] and Zn[**8a**] exhibit no splitting of the *ν*CN band at all.

The influence of the aromatic substituents, methyl or chloride, on the catalytic activity of most of the complexes is minor in the case of the symmetrically substituted nitrilo and ester ligands (*e.g.* Table 6, entries 7 and 8) and rather counterproductive in the case of the asymmetrically substituted as exemplified by entry 9 (Table 6) where the unsubstituted ligand still delivers the best results with 77% yield (entry 9: 77% for Zn[**1d**]; 46% for Zn[**2d**] and 51% for Zn[**3d**]). The same trend is found at a lower temperature, around 40 °C, and upon adjusting the amount of the catalyst (0.1 mol%) (entry 12: 79% for Zn[**1d**]; 51% for Zn[**2d**] and 78% for Zn[**3d**]). Correlating the different reactions summarized in Table 6, ligands displaying an *ortho*-phenylenediamine linker give a small advantage to the symmetrically substituted ligand with an ancillary ester function and dimethyl substitution at the aromatic, with a rough reactivity trend being accordingly: –Me ≳ –H > –Cl. Taking into account the diverse mechanisms found in the literature for the coupling of epoxide and CO_2[1,19] and DFT studies involving in particular zinc salphen,[24] a general mechanism can be proposed for the Zn–N_2O_2/(*n*-Bu)$_4$NI catalytic system (Scheme 5). Considering that the reports on ionic zinc salens of the type [N_2O_2Zn-I][NR_4] have been scarce, it seems reasonable to consider in our case a neutral Zn–N_2O_2 species as the starting point in the catalytic cycle. The first step to the formation of the cyclic carbonate involves basically the activation of the epoxide *via* coordination and ring opening to form a reactive metal-alkoxide, the actual active species in the catalytic cycle. Equivalent Zn salphen–epoxide educts have been structurally characterized by Kleij and coworkers.[25] The ammonium halide co-catalyst comes into play in the nucleophilic attack on the epoxide, hence supporting the formation of the reactive zinc alkoxide. The second step of the reaction would be the formation of a carbonate linkage *via* CO_2 insertion into the metal–alkoxide bond. This intermediate can either form a cyclic monomer *via* intramolecular rearrangement or a polycarbonate through further alternating insertions of epoxide and carbon dioxide molecules. In our case, the system tends to form exclusively cyclic carbonates,[9]



Scheme 4 Mesomeric forms of the Zn–N_2O_2 structure and analogy with zinc salphens.



Scheme 5 Mechanism proposed for the zinc–N_2O_2/NBu_4I catalytic system.

with the ammonium cation playing most probably a preponderant role in the cyclization of the carbonato species. More studies are in progress to understand the kinetics of the reaction and get more insight into the mechanism at work in this reaction.

Conclusions

We have synthesized a range of new zinc complexes displaying chelating N_2O_2 ligands with ancillary nitrilo and/or ester groups. These complexes were revealed to be highly effective in the production of PC, propylene carbonate, from propylene oxide and carbon dioxide. The coupling can be performed under mild reaction conditions and low catalyst loadings, with the utilization of tetrabutyl iodide as the co-catalyst being, however, obligatory for the success of the reaction. Some of the new complexes, based on symmetric ligands, two nitrilo-containing Zn[**2a**] and Zn[**3a**] and three malonato ligands Zn[**1b**], Zn[**2b**] and Zn[**3b**], could be for the first time structurally characterized *via* X-ray diffraction. In comparison to the results obtained with the "parent compound" Zn[**1a**], screening showed that the zinc complexes with *ortho*-phenylenediamino linkers actually work more efficiently than those with aliphatic or non-conjugated aromatic linkers. In addition, the presence of ester groups at the backbone of the ligand instead of nitrile groups leads to higher yield of PC. Within the range of the complexes displaying an *ortho*-phenylenediamino linker, the influence of aromatic substituents remains negligible.

Experimental

General

^{1}H- and ^{13}C-NMR spectra were recorded operating at 399.91 and 100.56 MHz, respectively, by means of a Varian Inova Unity 400 spectrometer (software VNMRJ 3.2) equipped with an Oxford Magnet (9.4 T). IR spectra were obtained using a Varian 660-IR FT-IR spectrometer. Mass spectra were measured using a Bruker ApexQe hybrid 9.4 T FT-ICR. Gel permeation chromatography (GPC) was performed using a PSS SDV 5μ 1000 Å and a PSS SDV 5μ 100 Å column of the company

Polymer Standard Service (PSS). The molecules were detected using a RI-Detector L-7490 (Merck). Tetrahydrofuran was used as an eluent and toluene as an internal standard. Data processing was done using the software PSS WINGPC 6 of the company PSS. For the determination of the glass transition temperature of the polycarbonates, differential scanning calorimetry was applied using a Mettler Toledo DSC822e. For inductively coupled plasma atomic emission spectroscopy (ICP-AES) a 720/725-ES emission spectrometer with a CCD detector from Agilent Technologies was used. The plasma was generated with a 40 MHz quartz-controlled generator where argon is the carrier gas. Elementary analysis was performed using a CHNS-Analyser from the company Elementar. UV-Vis spectra were measured using an MCS 501 UV-NIR (Zeiss). X-ray analyses were performed using a Bruker Apex II Quazar diffractometer. 2124 frames were collected with an irradiation time of 1 s per frame. Integration of the data proceeded with SAINT, the data were corrected for Lorentz and polarisation effects, and experimental absorption corrections with SADABS were performed.[26] For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used.[27] Crystallographic data were deposited at the Cambridge Crystallographic Database Centre (CCDC), supplementary publications no. CCDC complex Zn[**2a**]: 97320, Zn[**3a**]: 97319, Zn[**1b**]: 97318, Zn[**2b**]: 97321 and Zn[**3b**]: 97322. Figures were prepared using the appropriate Mercury software of the CCDC.[28]

The starting materials (*ortho*-phenylenediamine, ethyl (ethoxymethylene)cyanoacetate, methanol, dry tetrahydrofuran, epoxides, diethyl zinc solution (1 M in hexane) and the cocatalysts) were purchased from Sigma Aldrich. Except for the propylene oxide all of them were used without further purification. The epoxide was distilled from CaH_2 and stored under an argon atmosphere before using them in the catalytic tests.

Syntheses of the symmetric ligands

Procedure L-a. Two equivalents of ethyl 2-cyano-3-ethoxyacrylate or diethyl (ethoxymethylene)malonate were dissolved in hot methanol. Afterwards a solution of the diamine (also in methanol) was added and the reaction mixture was refluxed for 4 h. After cooling to −20 °C overnight a white solid precipitate was formed, which was collected by filtration, and washed with methanol and dried.

Procedure L-b. Same procedure as for L-a, but the reaction mixture was refluxed overnight before cooling down.

Procedure L-c. Same procedure as for L-a. The collected precipitate from the reaction mixture contained the products as well as the diamine. The latter was, in contrast to the product, not soluble in chloroform, so it can easily be separated by filtration.

Synthesis of the N_2O-ligands

Procedure L-d. One equivalent of the diamine was dissolved in hot methanol. Then another equivalent of ethyl 2-cyano-3-ethoxyacrylate or diethyl (ethoxymethylene)malonate (dissolved in methanol) was slowly added dropwise to the reaction mixture. When the two starting materials were combined, the mixture was refluxed for 4 h. The desired product was precipitated at −20 °C in the freezer. After collecting by filtration, it was washed with methanol and dried in vacuum.

Syntheses of the asymmetric ligands

Procedure L-e. One equivalent of ethyl 2-cyano-3-ethoxyacrylate or diethyl (ethoxymethylene)malonate was dissolved in hot methanol. Afterwards the N_2O-compound also dissolved in methanol was added. The reaction mixture was refluxed for 4 h and then cooled down to −20 °C. The solid precipitate was collected by filtration, washed with methanol and dried.

Procedure L-f. The procedure was applied similar to L-e, except the amount of ethyl 2-cyano-3-ethoxyacrylate or diethyl (ethoxymethylene)malonate was raised to excess and the reaction time was lengthened to refluxing overnight.

Procedure L-g. Instead of refluxing the reaction mixture for 4 h, the reaction time was extended to overnight. Everything else was done similar to procedure L-e.

Syntheses of the zinc complexes

Procedure Zn-a. Under an argon atmosphere the ligand was suspended or dissolved in THF. Then diethyl zinc solution (1 M in hexane) was added under stirring. The reaction mixture was stirred overnight and then the solvent was removed under reduced pressure leaving the zinc complex, which was further dried at 75 °C in vacuum.

Procedure Zn-b. The same procedure as for Zn-a was done, but after stirring the reaction mixture overnight a solid precipitate was formed. It was filtered under an argon atmosphere and dried at 75 °C under vacuum.

1a. 2-Propenoic acid, 3,3′-(1,2-phenylenediimino)bis[2-cyano-, diethyl ester] [CAS 59747-06-7] (diethyl 1,2-phenylenediimino-2-cyanoacrylate): procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (21.99 g, 130 mmol) and *ortho*-phenylenediamine (7.03 g, 65 mmol). Yield: white solid (22.95 g, 0.065 mmol, 92%). Mp = 193 °C. T_e = 201.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.31 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.22 (dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HH}$ = 5.7 Hz, 2H, CH_{aromat}), 7.32 (dd, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 5.8 Hz, 2H, CH_{aromat}), 7.75 (d, $^3J_{HH}$ = 12.8 Hz, 2H, CH), 10.82 (d, $^3J_{HH}$ = 12.6 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 61.8 (CH_2), 78.3 (=C_q), 117.2(C≡N), 120.1 (CH_{aromat}), 127.6 (CH_{aromat}), 130.9 ($C_{q,aromat}$), 153.6 (C–H), 167.4 (C=O). MS (ESI+) *m*/*z* (%): 355 (15) $[M + H]^+$, 372 (100) $[M + NH_4]^+$, 377 (16) $[M + Na]^+$. IR (KBr): ν = 3166 (m, ν_{N-H}), 2214 (s, $\nu_{C\equiv N}$), 1696, 1674, 1639, 1618, 1597 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 3.86; N, 15.81; found: C, 60.94; H, 5.21; N, 15.90. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 292 (31 990), 332 (25 750) nm (mol^{-1} dm^3 cm^{-1}).

1b. Propanedioic acid, 2,2′-[1,2-phenylenebis(iminomethylidyne)]bis-, 1,1′,3,3′-tetraethyl ester [CAS 4921-71-5] (malonic acid, [*o*-phenylenebis(iminomethylidyne)]di-, tetraethyl ester): procedure L-a with diethyl (ethoxymethylene)malonate (43.25 g, 200 mmol) and *ortho*-phenylenediamine (10.81 g,

100 mmol). Yield: yellow solid (30.34 g, 67.65 mmol, 68%). Mp = 94.4 °C. T_e = 78.2 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.29 (m, 12H, CH_3), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.26 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.21 (s, 4H, CH_{aromat}), 8.32 (d, $^3J_{HH}$ = 13 Hz, 2H, CH), 10.94 (d, $^3J_{HH}$ = 13.0 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.4, 14.6 (CH_3), 60.4, 60.8 (CH_2), 95.9 (=C_q), 120.1 (CH_{aromat}), 126.7 (CH_{aromat}), 131.9 ($C_{q,aromat}$), 153.5 (CH), 165.6, 168.8 (C=O). MS (ESI+) m/z (%): 449 (100) $[M + H]^+$, 471 (19) $[M + Na]^+$. IR (KBr): ν = 3137 (m, ν_{N-H}), 1720, 1696, 1658, 1618, 1582 (m, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{28}N_2O_8$: C, 58.92; H, 6.29; N, 6.25; found: C, 59.05; H, 6.533; N, 6.301. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 289 (30 500), 331 (26 000) nm (mol^{-1} dm^3 cm^{-1}).

1c. Procedure L-d with diethyl (ethoxymethylene)malonate and (10.00 g, 50.0 mmol), *ortho*-phenylenediamine (5.40 g, 50.0 mmol). Yield: white solid (9.79 g, 35.1 mmol, 70%). T_e = 89.2 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 3.73 (s, 2H, NH_2), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 4.28 (t, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 6.81 (m, 4H, CH_{aromat}), 7.01 (t, $^3J_{HH}$ = 7.6 Hz, 1H, CH_{aromat}), 7.08 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH_{aromat}), 8.39 (d, $^3J_{HH}$ = 13.6 Hz, 1H, CH), 10.81 (d, $^3J_{HH}$ = 13.5 Hz, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.21, 14.30 (CH_3), 59.83, 60.21 (CH_2), 93.15 (=C_q), 117.46 (CH_{aromat}), 118.99 (CH_{aromat}), 119.93 (CH_{aromat}), 126.32 (CH_{aromat}), 127.63 ($CH_{q,aromat}$), 137.85 ($CH_{q,aromat}$), 154.03 (CH), 165.55, 169.08 (C=O). MS: (ESI+) m/z (%): 279 (100) $[M + H]^+$, 579 (56) $[2M + Na]^+$. IR (KBr): ν = 3399, 3342 (m, ν_{N-H2}), 3259 (m, ν_{N-H}), 2214 (s, $\nu_{C\equiv N}$), 1593 (s), 1609 (m), 1658 (s), 1697, 1597 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07; found: C, 60.16; H, 6.61; N, 10.12. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 293 (9873), 332 (15 510) nm (mol^{-1} dm^3 cm^{-1}).

1d. Procedure L-e with ethyl 2-cyano-3-ethoxyacrylate (12.41 g, 71.9 mmol) and ligand **1c** (20.00 g, 71.9 mmol). Yield: white solid (27.97 g, 69.7 mmol, 97%). T_e = 138.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.29 (m, 9H, CH_3), 4.23 (m, 6H, CH_2), 7.20 (m, 4H, CH_{aromat}), 7.73 (d, $^3J_{HH}$ = 12.9 Hz, 4H, CH), 8.30 (d, $^3J_{HH}$ = 12.9 Hz, 4H, CH), 10.77 (d, $^3J_{HH}$ = 12.8 Hz, 4H, NH), 10.98 (d, $^3J_{HH}$ = 12.9 Hz, 4H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.13, 14.30 (CH_3), 60.19, 60.62, 61.39 (CH_2), 77.51 (=C_q), 95.96 (=C_q), 117.27 (C≡N), 119.56, 120.09 (CH_{aromat}), 126.55, 127.21 (CH_{aromat}), 130.56 ($C_{qaromat}$), 131.63 ($C_{q,aromat}$), 153.28 (CH), 153.45 (CH), 165.19, 168.64 (C=O), 167.09 (C=O). MS (ESI+) m/z (%): 402 (100) $[M + H]^+$, 424 (18) $[M + Na]^+$, 825 (31) $[2M + Na]^+$. IR (KBr): ν = 3200 (m, ν_{N-H}), 2217 (s, $\nu_{C\equiv N}$), 1589, 1630, 1649, 1684, 1716 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{23}N_3O_6$: C, 59.84; H, 5.78; N, 10.47; found: C, 59.87; H, 5.92; N, 10.68. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 291 (30 470), 332 (25 410) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (THF) λ_{max} (ε) = 291 (31 930), 328 (26 340) nm (mol^{-1} dm^3 cm^{-1}).

2a. Procedure L-c with ethyl 2-cyano-3-ethoxyacrylate (3.00 g, 16.9 mmol) and 4,5-dichloro-1,2-phenylenediamine (5.73 g, 33.9 mmol). Yield: grey-brown solid (2.19 g, 5.18 mmol, 31%). T_e = 204.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.37 (t, $^3J_{HH}$ = 7.1Hz, 6H, CH_3), 4.32 (q, $^3J_{HH}$ = 7.1Hz, 4H, CH_2), 7.32 (s, 2H, CH_{aromat}), 7.68 (d, $^3J_{HH}$ = 12.5 Hz, 2H, CH), 10.83 (d, $^3J_{HH}$ = 12.4 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 62.0 (CH_2), 79.7 (=C_q), 116.4 (C≡N), 121.2 (CH_{aromat}), 129.9 ($C_{q,aromat}$), 131.0 ($C_{q,aromat}$–Cl), 152.6 (CH), 167.0 (C=O). MS (ESI+) m/z (%): 440 (100) $[M + NH_4]^+$, 869 (11) $[2M + Na]^+$. IR (KBr): ν = 3178 (m, ν_{N-H}), 2216, 2231 (s, $\nu_{C\equiv N}$), 1595, 1618, 1645 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{16}Cl_2N_4O_4$: C, 51.08; H, 3.81; N, 13.24; found: C, 50.99; H, 3.82; N, 13.38. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 293 (34 710), 335 (27 660) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 291 (39 910), 325 (30 160) nm (mol^{-1} dm^3 cm^{-1}).

2b. Procedure L-b with diethyl (ethoxymethylene)malonate (2.3 ml, 11.30 mmol) and 4,5-dichloro-1,2-phenylenediamine (500 mg, 2.82 mmol). Yield: grey needles (1.15 g, 2.22 mmol, 78%). T_e = 137.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.34 (m, 12H, CH_3), 4.26 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 4.30 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.33 (s, 2H, CH_{aromat}), 8.25 (d, $^3J_{HH}$ = 12.7 Hz, 2H, CH), 11.01 (d, $^3J_{HH}$ = 12.6 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.17, 14.35 (CH_3), 60.45, 60.84 (CH_2), 97.18 (=C_q), 120.93 (CH), 129.73 ($C_{q,aromat}$–Cl), 130.97 ($C_{q,aromat}$), 152.20 (CH), 165.04, 168.48 (C=O). MS (ESI +) m/z (%): 516 (100) $[M + H]^+$, 539 (53) $[M + Na]^+$, 1054 (71) $[2M + Na]^+$. HR-MS (ESI+) m/z: anal. calcd. for $C_{22}H_{27}Cl_2N_2O_8$: 517.11390; found: 517.11761. IR (KBr): ν = 3169 (m, ν_{N-H}), 1583, 1630, 1648, 1688, 1703 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{26}Cl_2N_2O_8$: C, 51.07; H, 5.07; N, 5.41; found: C, 50.87; H, 5.02; N, 5.31. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 291 (40 330), 335 (32 400) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (THF): λ_{max} (ε) = 245 (6661), 292 (40 780), 335 (32 360) nm (mol^{-1} dm^3 cm^{-1}).

2c. Procedure L-d with diethyl (ethoxymethylene)malonate (3.11 g, 14.4 mmol) and 4,5-dichloro-1,2-phenylenediamine (97%) (2.63 g, 14.4 mmol). Yield: reddish black crystals (3.52 g, 10.14 mmol, 70%), T_e = 163.1 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 3.74 (s, 2H, NH_2), 4.24 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 4.30 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 6.89 (s, 1H, CH_{aromat}), 7.16 (s, 1H, CH_{aromat}), 8.28 (d, $^3J_{HH}$ = 13.2 Hz, 1H, CH), 10.74 (d, $^3J_{HH}$ = 13.0 Hz, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.25, 14.39 (CH_3), 60.23, 60.59 (CH_2), 94.93 (=C_q), 118.30 (CH_{aromat}), 120.39 (CH_{aromat}), 122.63, 127.25, 129.31, 137.40 ($C_{q,aromat}$), 153.26 (CH), 165.28 (C=O), 169.09 (C=O). MS (ESI+) m/z (%): 347 (100) $[M + H]^+$, 717 (52), $[2M + Na]^+$. IR (KBr): ν = 3344, 3396 (m, ν_{N-H2}), 3247 (w, ν_{N-H}), 1589, 1609, 1666, 1700 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{16}Cl_2N_2O_4$: C, 48.43; H, 4.64; N, 8.07; found: C, 48.49; H, 4.77; N, 8.13. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 250 (12 040), 299 (11 500), 341 (14 370) nm (mol^{-1} dm^3 cm^{-1}).

2d. Procedure L-f with ethyl 2-cyano-3-ethoxyacrylate (2, 92 g, 17, 28 mmol) and ligand **2c** (2.00 g, 5.76 mmol). Yield: grey needles (2.54 g, 5.39 mmol, 94%). T_e = 146.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.34 (m, 9H, CH_3), 4.28 (m, 6H, CH_2), 7.29 (s, 1H, CH_{aromat}), 7.36 (s, 1H, CH_{aromat}), 7.68 (d, $^3J_{HH}$ = 12.6 Hz, 1H, CH), 8.24 (d, $^3J_{HH}$ = 12.6 Hz, 1H, CH), 10.80 (d, $^3J_{HH}$ = 12.5 Hz, 1H, NH), 11.04 (d, $^3J_{HH}$ = 12.3 Hz, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.08, 14.27 (CH_3), 60.50, 60.92, 61.74 (CH_2), 79.20 (=C_q), 97.60 (=C_q), 116.53 (C≡N),

121.00, 121.12 (CH_{aromat}), 129.73 ($C_{q,aromat}$), 129.84, 130.80 ($C_{q,aromat}$–Cl), 131.09 ($C_{q,aromat}$), 152.02 (CH), 152.65 (CH), 164.89, 168.56 (C═O), 166.92 (C═O). MS (ESI+) *m*/*z* (%): 470 (100) $[M + H]^+$, 492 (23) $[M + Na]^+$, 963 (20) $[2M + Na]^+$. IR (KBr): ν = 3173 (m, $\nu_{N–H}$), 2219 (m, $\nu_{C\equiv N}$), 1586, 1611, 1636, 1691 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{21}Cl_2N_3O_6$: C, 51.08; H, 4.50; N, 8.93; found: C, 50.97; H, 4.55; N, 8.89. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 292 (37 530), 336 (30 080) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 204 (26 180), 290 (40 360), 331 (30 280) nm (mol^{-1} dm^3 cm^{-1}).

3a. Procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (7.08 g, 42 mmol), 4,5-dimethyl-1,2-phenylenediamine (3.00 g, 21 mmol). Yield: white solid (6.78 g, 17.73 mmol, 84%). T_e = 190.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 2.28 (s, 6H, C_{aromat}–CH_3), 4.29 (q, $^3J_{HH}$ = 4 Hz, 7.1H, CH_2), 6.97 (s, 2H, CH_{aromat}), 7.70 (d, $^3J_{HH}$ = 2 Hz, 12.9H, CH), 10.70 (d, $^3J_{HH}$ = 12.9 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 19.5 (C_{aromat}–CH_3), 61.5 (CH_2), 77.3 (═C_q), 117.4 (C≡N), 121.1 (CH_{aromat}), 128.2 ($C_{q,aromat}$), 136.6 ($C_{q,aromat}$–CH_3), 153.7 (CH), 167.4 (C═O). MS (ESI+) *m*/*z* (%): 400 (100) $[M + NH_4]^+$, 787 (29) $[2M + Na]^+$. IR (KBr): ν = 3200 (m, $\nu_{N–H}$), 2215 (s, $\nu_{C\equiv N}$), 1604, 1635, 1671 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{22}N_4O_4$: C, 62.82; H, 5.80; N, 14.65; found: C, 62.90; H, 6.052; N, 14.90. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 294 (31 820), 335 (25 880) nm (mol^{-1} dm^3 cm^{-1}).

3b. Propanedioic acid, 2,2′-[(4,5-dimethyl-1,2-phenylene)bis(iminomethylidyne)]bis-, tetraethyl ester [CAS 79852-83-8]: procedure L-b with diethyl (ethoxymethylene)malonate (15.04 g, 14.06 ml, 69.6 mmol) and 4,5-dimethyl-1,2-phenylenediamine (4.74 g, 34.8 mmol). Yield: white solid (10.47 g, 22.0 mmol, 63%). T_e = 107.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 2.27 (s, 6H, C_{aromat}–CH_3), 4.27 (m, 8H, CH_2), 7.01 (s, 2H, CH_{aromat}), 8.33 (d, $^3J_{HH}$ = 13.2 Hz, 2H, CH), 10.88 (d, $^3J_{HH}$ = 13.2 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.23, 14.36 (CH_3), 19.8 ($C_{q,aromat}$–CH3), 60.08, 60.41 (CH_2), 94.94 (═C_q), 121.03 (CH_{aromat}), 129.21 ($C_{q,aromat}$), 135.34 ($C_{q,aromat}$–CH_3), 153.68 (CH), 165.65, 168.57 (C═O). MS (ESI+) *m*/*z* (%): 477 (100) $[M + H]^+$, 499 (9) $[M + Na]^+$, 515 (3) $[M + K]^+$, 975 (14) $[2M + Na]^+$. IR (KBr): ν = 3179 (m, $\nu_{N–H}$), 1585, 1625, 1646, 1671, 1681, 1711 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{24}H_{32}N_2O_8$: C, 60.49; H, 6.77; N, 5.88; found: C, 60.70; H, 6.99; N, 5.913. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 293 (31 290), 335 (25 770) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (THF): λ_{max} (ε) = 292 (32 350), 332 (26 680) nm (mol^{-1} dm^3 cm^{-1}).

3c. Procedure L-d with ethyl 2-cyano-3-ethoxyacrylate (3.33 g, 19.3 mmol) and 4,5-dimethyl-1,2-phenylenediamine (2.76 g, 9.3 mmol). Yield: white solid (3.56 g, 13.7 mmol, 71%). T_e = 154.4 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 2.18 (s, 6H, C_{aromat}–CH_3), 3.44 (s, 2H, NH_2), 4.28 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 6.62 (s, 1H, CH_{aromat}), 6.79 (s, 1H, CH_{aromat}), 7.71 (d, $^3J_{HH}$ = 13.5 Hz, 1H, CH), 10.54 (d, $^3J_{HH}$ = 13.0 Hz, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.30 (CH_3), 18.93, 19.31 (C_{aromat}–CH_3), 61.00 (CH_2), 74.45 (═C_q), 118.19 (C≡N), 119.68 (CH_{aromat}), 120.08 (CH_{aromat}), 124.88 ($C_{q,aromat}$), 128.84 ($C_{q,aromat}$–CH_3), 135.13 ($_{Cq,aromat}$), 135.70 ($C_{q,aromat}$–CH_3), 153.92 (CH), 167.83 (C═O). MS (ESI+) *m*/*z* (%): 260 (43) $[M + H]^+$, 277 (100) $[M + NH_4]^+$, 282 (6) $[M + Na]^+$, 519 (42) $[2M + H]^+$, 541 (19) $[2M + Na]^+$. IR (KBr): ν = 3293, 3353 (m, $\nu_{N–H2}$), 3139 (m, $\nu_{N–H}$), 2211 (s, $\nu_{C\equiv N}$), 1514, 1624, 1673 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{17}N_3O_2$: C, 64.85; H, 6.61; N, 16.20; found: C, 64.61; H, 6.59; N, 16.44. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 264 (6402), 300 (8999), 345 (14 240) nm (mol^{-1} dm^3 cm^{-1}).

3d. Procedure L-g with diethyl (ethoxymethylene)malonate (0.24 g, 1.20 mmol) and ligand **3c** (310 mg, 1.20 mmol). Yield: white solid (0.36 g, 0.84 mmol, 70%). T_e = 114.5 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.32 (m, 9H, CH_3), 2.27 (s, 3H, C_{aromat}–CH_3), 2.29 (s, 3H, C_{aromat}–CH_3), 4.26 (m, 5H, CH_2), 6.97 (s, 1H, CH_{aromat}), 7.03 (s, 1H, CH_{aromat}), 7.77 (d, $^3J_{HH}$ = 14.3 Hz, 1H, NH), 8.17 (d, $^3J_{HH}$ = 14.2 Hz, 1H, CH), 8.32 (d, $^3J_{HH}$ = 13.1 Hz, 1H, CH), 10.94 (d, $^3J_{HH}$ = 12.7 Hz, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.13, 14.28 (CH_3), 19.25, 19.45 (C_{aromat}–CH_3), 60.19, 60.63, 61.17 (CH_2), 78.85 (═C_q), 95.36 (═C_q), 115.09 (C≡N), 120.72 (CH_{aromat}), 122.90 (CH_{aromat}), 127.86 ($C_{q,aromat}$), 129.87 ($C_{q,aromat}$), 135.36, 136.80 ($C_{q,aromat}$–CH_3), 153.26 (CH), 154.23 (CH), 164.18, 165.53, 168.82 (C═O). MS (ESI+) *m*/*z* (%): 430 (100) $[M + H]^+$, 859 (32) $[2M + H]^+$. HR-MS (ESI+) *m*/*z*: anal. calcd. for $C_{22}H_{28}N_3O_6$: 430.19726; found: 430.19781; anal. calcd. for $C_{44}H_{55}N_6O_{12}$: 859.38725; found: 859.39065. IR (KBr): ν = 3198 (w, $\nu_{N–H}$), 2212 (s, $\nu_{C\equiv N}$), 1595, 1631, 1698 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{27}N_3O_6$: C, 61.53; H, 6.34; N, 9.78; found: C, 61.31; H, 6.48; N, 9.76. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 294 (30 040), 335 (23 730) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 291 (27 210), 330 (22 090) nm (mol^{-1} dm^3 cm^{-1}).

4a. Procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (14.00 g, 82.8 mmol) and 1,2-ethylenediamine (2.8 ml, 41.4 mmol). Yield: white solid (10 g, 32.7 mmol, 79%). T_e = 147.7 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 3.53 (m, 4H, CH_2–CH_2), 4.27 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.29 (s, 2H, CH), 9.00 (d, $^3J_{HH}$ = 11.6 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.25 (CH_3), 49.82 (CH_2–CH_2), 61.12 (CH_2), 73.78 (═C_q), 117.74 (C≡N), 159.16 (CH), 167.75 (C═O). MS (ESI+) *m*/*z* (%): 307 (31) $[M + H]^+$, 329 (100) $[M + Na]^+$. IR (KBr): ν = 3288 (m, $\nu_{N–H}$), 2204 (s, $\nu_{C\equiv N}$), 1681, 1612 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29; found: C, 54.85; H, 6.00; N, 18.56. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 277 (26 730), 294 (26 890) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 201 (21 320), 275 (29 570), 292 (28 690) nm (mol^{-1} dm^3 cm^{-1}).

4b. Procedure L-a with diethyl (ethoxymethylene)malonate (12.45 g, 57.6 mmol) and 1,2-ethylenediamine (1.72 g, 28.8 mmol). Yield: white solid (10.09 g, 28.8 mmol, 99%). T_e = 122.5 °C. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.20 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 3.48 (m, 4H, N–CH_2), 4.07 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.89 (d, $^3J_{HH}$ = 13.9 Hz, 2H, CH), 9.14 (d, $^3J_{HH}$ = 13.3 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, CD_2Cl_2): δ = 14.43, 14.48 (CH_3), 50.06 (CH_2–CH_2), 59.83, 60.11 (CH_2), 91.29 (═C_q), 160.07 (CH), 165.72, 169.20 (C═O). MS (ESI+) *m*/*z* (%): 401 (100) $[M + H]^+$, 423 (11) $[M + Na]^+$, 824 (13) $[2M + Na]^+$. IR (KBr):

ν = 3266 (m, ν_{N-H}), 1698, 1659, 1602 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{26}N_2O_8$: C, 53.99; H, 7.05; N, 7.00; found: C, 53.82; H, 7.27; N, 6.98. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 274 (25 040), 293 (27 220) nm (mol^{-1} dm^3 cm^{-1}).

5a. 2-Propenoic acid, 3,3′-(1,2-ethanediyldiimino)bis[2-cyano-, 1,1′-diethyl ester] [CAS 92325-24-1]: procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (21.14 g, 125 mmol) and 1,3-diaminopropane (5.2 ml, 62 mmol). Yield: white solid (15.58 g, 48.62 mmol, 74%). Mp = 108.5 °C. T_e = 110.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (m, 6H, CH_3), 1.94 (p, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2–CH_2–CH_2), 3.43 (m, 4H, N–CH_2), 4.20 (m, 2H, CH_2), 7.07 (m, 1H, NH), 7.37 (m, 1H, CH), 7.84 (m, 1H, CH), 8.93 (m, 1H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.29, 14.40 (CH_3), 31.25 (–CH_2–CH_2–CH_2), 46.25, 46.47 (–N–CH_2), 60.71, 60.80 (CH_2), 71.92, 72.25, 72.66, 72.72 (=C_q), 116.72, 116.76, 118.38, 118.54 (C≡N), 159.15, 159.31 (CH), 165.02 (C=O), 167.90 (C=O). MS (ESI+) *m/z* (%): 321 (36) $[M + H]^+$, 343 (100) $[M + Na]^+$. IR (KBr): ν = 3280 (m, ν_{N-H}), 2208 (s, $\nu_{C\equiv N}$), 1689, 1635 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{15}H_{20}N_4O_4$: C, 55.92; H, 6.38; N, 17.64; found: C, 56.24; H, 6.29; N, 17.49. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 288 (30 760) nm (mol^{-1} dm^3 cm^{-1}).

5b. Propanedioic acid, 2,2′-[(1,2-ethanediyl)bis(iminomethylidyne)]bis-, 1,1′,3,3′-tetraethyl ester [CAS 14452-46-1] (malonic acid, [ethylenebis(iminomethylidyne)]di-,tetraethyl ester): procedure L-a with diethyl (ethoxymethylene)malonate (10.43 g, 48.2 mmol) and 1,3-diaminopropane (1.79 g, 24.1 mmol). Yield: white solid (6.38 g, 15.4 mmol, 64%). T_e = 97.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.90 (q, $^3J_{HH}$ = 6.92 Hz, 2H, CH_2–CH_2–CH_2), 3.39 (q, $^3J_{HH}$ = 6.7 Hz, 4H, N–CH_2), 4.14 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.19 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.93 (d, $^3J_{HH}$ = 13.9 Hz, 2H, CH), 9.19 (m, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.21, 14.30 (CH_3), 31.54 (N–CH_2), 46.34 (CH_2–CH_2–CH_2), 59.59, 59.86 (CH_2), 90.26 (=C_q), 159.66 (CH), 165.63, 169.29 (C=O). MS (ESI+) *m/z* (%): 415 (100) $[M + H]^+$, 437 (17) $[M + Na]^+$, 851 (13) $[2M + Na]^+$. IR (KBr): ν = 3266 (m, ν_{N-H}), 1697, 1663, 1605 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{19}H_{30}N_2O_8$: C, 55.06; H, 7.30; N, 6.76; found: C, 55.12; H, 7.42; N, 6.90. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 288 (31 510) nm (mol^{-1} dm^3 cm^{-1}).

6a. 2-Propenoic acid, 3,3′-(1,3-propanediyldiimino)bis[2-cyano-, diethyl ester] [CAS 157737-86-5]: procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (8.12 g, 48 mmol) and 1,4-diaminobutane (2.4 ml, 24 mmol). Yield: white solid (6.05 g, 18.09 mmol, 75%). T_e = 166.7 °C. ^{1}H-NMR (400 MHz, $SO(CH_3)_2$): δ = 1.15 (m, 6H, CH_3), 1.43 (m, 4H, CH_2–CH_2–CH_2), 3.26 (m, 4H, N–CH_2), 4.06 (m, 4H, CH_2), 7.73 (d, $^3J_{HH}$ = 14.5 Hz, 6H, CH), 7.91 (d, $^3J_{HH}$ = 15.0 Hz, 6H, CH), 8.63 (d, $^3J_{HH}$ = 14.7 Hz, 6H, NH), 9.07 (d, $^3J_{HH}$ = 14.3 Hz, 6H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CH_3)_2$): δ = 14.24, 14.34 (CH_3), 26.85 (CH_2–CH_2–CH_2), 48.35 (N–CH_2), 59.46 (CH_2), 68.13, 68.86 (=C_q), 116.82, 119.15 (C≡N), 159.50, 159.96 (CH), 165.09, 166.60 (C=O). MS (ESI+) *m/z* (%): 335 (38) $[M + H]^+$, 357 (100) $[M + Na]^+$. IR (KBr): ν = 3273, 3227 (s, ν_{N-H}), 2205 (s, $\nu_{C\equiv N}$), 1690, 1623, 1540 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{16}H_{22}N_4O_4$: C, 57.47; H, 6.63; N, 16.76; found: C, 57.32; H, 6.83; N, 16.94. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (32 900) nm (mol^{-1} dm^3 cm^{-1}).

6b. Propanedioic acid, 2,2′-[1,3-propanediylbis(imino methylidyne)]bis-, 1,1′,3,3′-tetraethyl ester [CAS 1415327-35-3]: procedure L-a with diethyl (ethoxymethylene)malonate (22.37 g, 20.9 ml, 103.5 mmol) and 1,4-diaminobutane (4.56 g, 51.7 mmol). Yield: white solid (18.89 g, 44.09 mmol, 85%). T_e = 136.3 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.62 (s, 4H, CH_2–CH_2–CH_2), 3.32 (d, $^3J_{HH}$ = 5.4 Hz, 4H, N–CH_2), 4.12 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 14.3 Hz, 4H, CH_2), 4.18 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 14.3 Hz, 4H, CH_2), 7.92 (d, $^3J_{HH}$ = 14.0 Hz, 2H, CH), 9.18 (m, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.19, 14.29 (CH_3), 27.69 (CH_2–CH_2–CH_2), 49.10 (N–CH), 59.49, 59.73 (CH_2), 89.67 (=C_q), 159.74 (CH), 165.81, 169.28 (C=O). MS (ESI+) *m/z* (%): 429 (100) $[M + H]^+$, 451 (42) $[M + Na]^+$. IR (KBr): ν = 3303 (m, ν_{N-H}), 1597, 1629, 1678 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{32}N_2O_8$: C, 56.06; H, 7.53; N, 6.54; found: C, 55.99; H, 7.50; N, 6.60. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (35 560) nm (mol^{-1} dm^3 cm^{-1}).

7a. 2-Propenoic acid, 3,3′-(1,2-cyclohexanediyldiimino)bis[2-cyano-, diethyl ester, *trans*-] [CAS 156996-20-2]: procedure L-a with ethyl 2-cyano-3-ethoxyacrylate (4.06 g, 24 mmol) and 1,2-diaminocyclohexane (1.4 ml, 12 mmol). Yield: white solid (3.37 g, 9.35 mmol, 78%). Mp = 167.8 °C. T_e = 171.9 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.37 (m, 4H, CH_{cyclo}, $CH_{2,cyclo}$), 1.81 (d, $^3J_{HH}$ = 7.92 Hz, 2H, $CH_{2,cyclo}$), 2.06 (d, $^3J_{HH}$ = 12.6 Hz, 2H, $CH_{2,cyclo}$), 3.00 (m, 2H, CH_{cyclo}), 4.17 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.20 (d, $^3J_{HH}$ = 13.6 Hz, 2H, CH), 8.81 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 11.8 Hz, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.5 (CH_3), 24.3 ($CH_{2,cyclo}$), 32.4 ($CH_{2,cyclo}$), 61.2 (CH_2), 64.0 (CH_{cyclo}), 72.9 (=C_q), 118.3 (C≡N), 158.3 (CH), 168.1 (C=O). MS (ESI+) *m/z* (%): 361 (100) $[M + H]^+$, 383 (97) $[M + Na]^+$, 743 $[2M + H]^+$. IR (KBr): ν = 3274 (m, ν_{N-H}), 2210 (s, $\nu_{C\equiv N}$), 1683, 1630 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{24}N_4O_4$: C, 59.99; H, 6.71; N, 15.55; found: C, 60.38; H, 6.583; N, 15.53. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 277 (30 750) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 203 (20 740), 275 (38 180) nm (mol^{-1} dm^3 cm^{-1}).

7b. Procedure L-a with diethyl (ethoxymethylene)malonate (9.56 g, 44.2 mmol) and 1,2-diaminocyclohexane (2.52 g, 2.1 mmol). Yield: orange-white solid (7.75 g, 17.13 mmol, 78%). T_e = 109.6 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.29 (d, $^3J_{HH}$ = 10.6 Hz, 2H, $CH_{2,cyclo}$), 1.38 (m, 2H, $CH_{2,cyclo}$), 1.78 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $CH_{2,cyclo}$), 2.06 (d, $^3J_{HH}$ = 13.1 Hz, 2H, $CH_{2,cyclo}$), 2.97 (m, 2H, CH_{cyclo}), 4.05 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.14 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.82 (t, $^3J_{HH}$ = 13.8 Hz, 2H, CH), 9.14 (m, 2H, NH). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 14.18, 14.21 (CH_3), 24.12 ($CH_{2,cyclo}$), 32.19 ($CH_{2,cyclo}$), 59.43, 59.78 (CH_2), 63.51 (CH_{cyclo}), 90.36 (=C_q), 158.70 (CH), 165.31, 169.31 (C=O). MS (ESI+) *m/z* (%): 455 (100) $[M + H]^+$, 932 (15) $[2M + H]^+$. IR (KBr): ν = 3258 (m, ν_{N-H}), 1717, 1681, 1640, 1613 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{34}N_2O_8$: C, 58.14; H, 7.54; N, 6.16; found: C, 58.12; H, 7.55; N, 6.15. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 274 (31 120), 290 (19 760) nm (mol^{-1} dm^3 cm^{-1}).

8a. Procedure L-b with ethyl 2-cyano-3-ethoxyacrylate (27.70 g, 163.7 mmol) and 2-aminobenzylamine (10.00 g,

81.9 mmol). Yield: white solid (20.6 g, 56.0 mmol, 68%). T_e = 179.70 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.32 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 4.17 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 4.28 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 4.54 (d, $^3J_{HH}$ = 5.3 Hz, 2H, N–CH_2), 6.29 (d, $^3J_{HH}$ = 16.8 Hz, 1H, NH), 7.22 (m, 3H, CH_{aromat}), 7.29 (d, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{aromat}), 7.44 (t, $^3J_{HH}$ = 7.7 Hz, 1H, CH_{aromat}), 7.85 (d, $^3J_{HH}$ = 12.8 Hz, 1H, CH), 7.93 (d, $^3J_{HH}$ = 14.9 Hz, 1H, CH), 11.12 (d, $^3J_{HH}$ = 12.6 Hz, 1H, NH).^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 14.20, 14.23 (CH_3), 49.97 (N–CH_2), 61.83, 60.90 (CH_2), 77.14 (=C_q), 73.24 (C≡N), 116.89 (CH_{aromat}), 117.99 (C≡N), 117.16 (=C_q), 124.87 ($C_{q,aromat}$), 126.16 (CH_{aromat}), 130.71, 130.85 (CH_{aromat}), 137.09 ($C_{q,aromat}$), 152.28 (CH), 159.01 (CH), 167.73 (C=O), 167.79 (C=O). HR-MS (ESI+) *m/z*: anal. calcd. for $C_{19}H_{20}N_4O_4$: 368.1485; found: 368.1427. IR (KBr): ν = 3270 (m, ν_{N-H}), 2208 (s, $\nu_{C\equiv N}$), 1696 (s), 1641 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 15.21; found: C, 62.02; H, 5.56; N, 15.43. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 285 (28 440), 322 (21 070) nm (mol^{-1} dm^3 cm^{-1}). UV/Vis (MeCN): λ_{max} (ε) = 200 (28 530), 287 (32 640) nm (mol^{-1} dm^3 cm^{-1}).

8b. Procedure L-a with diethyl (ethoxymethylene)malonate (27.70 g, 16.5 ml, 81.85 mmol) and 2-aminobenzylamine (5.00 g, 40.93 mmol). Yield: yellowish solid (15.94 g, 34.46 mmol, 84%). T_e = 113.0 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (m, 12H, CH_3), 4.22 (m, 8H, CH_2), 4.57 (d, $^3J_{HH}$ = 5.6 Hz, 2H, N–CH_2), 7.18 (t, $^3J_{HH}$ = 7.5 Hz, 1H, CH_{aromat}), 7.27 (d, $^3J_{HH}$ = 7.3 Hz, 2H, CH_{aromat}), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 1H, CH_{aromat}), 8.10 (d, $^3J_{HH}$ = 13.9 Hz, 1H, CH), 8.47 (d, $^3J_{HH}$ = 13.0 Hz, 1H, CH), 9.36 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 7.0 Hz, 1H, NH), 11.31 (d, $^3J_{HH}$ = 13.0 Hz, 1H, NH). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 14.19–14.33 (CH_3), 49.32 (N–CH_2), 59.61–60.55 (CH_2), 91.12 (=C_q), 94.65 (=C_q), 116.97 (CH_{aromat}), 125.33 (CH_{aromat}), 126.12 ($C_{q,aromat}$), 129.26 (CH_{aromat}), 129.84 (CH_{aromat}), 137.52 ($C_{q,aromat}$), 152.50 (CH), 159.84 (CH), 165.30–169.24 (C=O). MS (ESI+) *m/z* (%): 463 (100) [M + H]$^+$, 485 (29) [M + Na]$^+$, 948 (17) [2M + Na]$^+$. IR (KBr): ν = 3281 (m, ν_{N-H}), 1589, 1615, 1641, 1665, 1693 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{23}H_{30}N_2O_8$: C, 59.73; H, 6.54; N, 6.06; found: C, 59.63; H, 6.75; N, 6.16. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 287 (24 570), 320 (19 420) nm (mol^{-1} dm^3 cm^{-1}).

Zn[1a]. Procedure Zn-a with ligand **1a** (5.00 g, 14.11 mmol), THF (75 ml) and diethylzinc in hexane (1 M) (14.1 ml, 14.11 mmol). Yield: yellow solid (5.88 g, 14.08 mmol, 99%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.29 (tr, $^3J_{HH}$ = 7.1Hz, 6H, CH_3), 4.25 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.05 (dd, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 6.1 Hz, 2H, CH_{aromat}), 7.56 (dd, $^3J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 6.1 Hz, 2H, CH_{aromat}), 8.35 (s, 2H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.1 (CH_3), 60.2 (CH_3), 68.1 (=C_q), 114.9 (CH_{aromat}), 121.2 (C≡N), 124.4 (CH_{aromat}), 138.0 ($C_{q,aromat}$), 156.3 (CH), 170.8 (C=O). MS (ESI+) *m/z* (%): 355 (17) [Lig + H]$^+$, 377 (40) [Lig + Na]$^+$, 417 (100) [M + H]$^+$, 833 (13) [2M + H]$^+$. MS (ESI−) *m/z* (%): 353 (13) [Lig − H]$^-$, 475 (100) [M + CH_3COO]$^-$, 893 (28) [2M + CH_3COO]$^-$. HR-MS (ESI+) *m/z*: anal. calcd. for $C_{18}H_{16}N_4O_4Zn$: 416.04575; found: 416.04612; anal. calcd. for $C_{18}H_{16}N_4NaO_4Zn$: 439.03552; found: 439.03590; anal. calcd. for $C_{18}H_{16}N_4O_4Zn$: 417.05468; found: 417.05474. IR (KBr): ν = 1549, 1592, 1625 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2203 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{16}N_4O_4Zn$: C, 51.75; H, 3.86; N, 13.41; found: C, 51.60; H, 4.05; N, 13.47. Anal. calcd. for $C_{18}H_{16}N_4O_4Zn$: Zn, 15.65; found: Zn, 15.62. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 241 (16 522), 307 (27 550), 360 (23 931) nm (mol^{-1} dm^3 cm^{-1}).

Zn[1b]. Procedure Zn-a with ligand **1b** (2.00 g, 4.46 mmol), THF (40 ml) and diethylzinc in hexane (1 M) (4.5 ml, 4.46 mmol). Yield: dark green solid (2.28 g, 4.45 mmol, 99%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.09 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.25 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.09 (dd, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 6.0 Hz, 2H, CH_{aromat}), 7.36 (dd, $^3J_{HH}$ = 3.4 Hz, $4J_{HH}$ = 6.0 Hz, 2H, CH_{aromat}), 8.91 (s, 2H, CH). ^{13}C{^{1}H}NMR (100 MHz, $SO(CD_3)_2$): δ = 14.27, 14.42 (CH_3), 58.58, 59.98 (CH_2), 87.79 (=C_q), 114.39 (CH_{aromat}), 124.34 (CH_{aromat}), 139.42 ($C_{q,aromat}$), 158.46 (CH), 166.76, 171.33 (C=O). MS (ESI+) *m/z* (%): 449 (99) [Lig + H]$^+$, 471 (100) [Lig + Na]$^+$, 511 (10) [M + H]$^+$. MS (ESI−) *m/z* (%): 447 (32) [Lig − H]$^-$, 569 (100) [M + CH_3COO]$^-$, 1079 (8) [2M + CH_3COO]$^-$. HR-MS (ESI+) *m/z*: anal. calcd. for $C_{22}H_{26}N_2O_8Zn$: 511.10534; found: 511.10607. IR (KBr): ν = 1525, 1584, 1606, 1673 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{26}N_2O_8ZnOH$: C, 49.97; H, 5.15; N, 5.30; found: C, 50.27; H, 5.38; N, 5.40. ICP-AES: anal. calcd. for $C_{22}H_{26}N_2O_8Zn$: Zn, 12.77; found: Zn, 13.04. REM-EDX: anal. calcd. for $C_{22}H_{26}N_2O_8Zn$: Zn, 12.77; found: Zn, 12.21. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (12 210), 313 (24 720), 346 (20 620) nm (mol^{-1} dm^3 cm^{-1}).

Zn[1d]. Procedure Zn-a with ligand **1d** (750 mg, 1.87 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.9 ml, 1.87 mmol). Yield: yellow solid (0.86 g, 1.84 mmol, 99%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.30 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 4.09 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 4.25 (m, 4H, CH_2), 7.04 (dt, $^3J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 7.7 Hz, 1H, CH_{aromat}), 7.10 (dt, $^3J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 6.9 Hz, 2H, CH_{aromat}), 7.34 (d, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{aromat}), 7.58 (d, $^3J_{HH}$ = 6.9 Hz, 1H, CH_{aromat}), 8.39 (s, 1H, CH), 8.89 (s, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.27, 14.35, 14.42 (CH_3), 58.58, 59.94, 60.57 (CH_2), 68.24 (=C_q), 87.92 (=C_q), 114.40 (CH_{aromat}), 115.16 (CH_{aromat}), 121.30 (C≡N), 124.06 (CH_{aromat}), 124.92 (CH_{aromat}), 138.27 ($C_{q,aromat}$), 139.45 ($C_{q,aromat}$), 156.74 (CH), 158.36 (CH), 166.85, 171.20, 171.25 (C=O). MS (ESI+) *m/z* (%): 402 (13) [Lig + H]$^+$, 424 (100) [Lig + Na]$^+$, 464 (10) [M + H]$^+$. MS (ESI−) *m/z* (%): 400 (41) [Lig − H]$^-$, 522 (100) [M + CH_3COO]$^-$, 863 (6) [M + Lig − H]$^-$, 985 (13) [2M + CH_3COO]$^-$. HR-MS (ESI+) *m/z*: anal. calcd. for $C_{20}H_{22}N_3O_6Zn$: 464.08056; found: 464.08086; anal. calcd. for $C_{20}H_{21}N_3NaO_6Zn$: 486.06140; found: 486.06198; anal. calcd. for $C_{21}H_{24}N_3O_7Zn$: 494.09112; found: 494.09100. IR (KBr): ν = 1546, 1589, 1613, 1671 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2205 (m, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{21}N_3O_6Zn$: C, 51.68; H, 4.55; N, 9.04; found: C, 51.25; H, 4.74; N, 9.03. ICP-AES: anal. calcd. for $C_{20}H_{21}N_3O_6Zn$: Zn, 14.07; found: Zn, 14.23. UV/Vis (MeCN): λ_{max} (ε) = 251 (13 364), 311 (25 696), 359 (22 715) nm (mol^{-1} dm^3 cm^{-1}).

Zn[2a]. Procedure Zn-b with ligand **2a** (750 mg, 1.77 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.8 ml, 1.80 mmol). Yield: beige solid (0.60 g, 1.23 mmol, 69%). ^{1}H-

NMR (400 MHz, $SO(CD_3)_2$): δ = 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.25 (q, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 7.89 (s, 2H, CH_{aromat}), 8.43 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.31 (CH_3), 60.61 (CH_3), 69.46 (=C_q), 116.94 (CH_{aromat}), 121.03 (C≡N), 126.11 ($C_{q,aromat}$–Cl), 138.48 ($C_{q,aromat}$), 157.67 (C=O), 170.70 (C=O). MS (ESI−) *m*/*z* (%): 421 (12) [Lig − H]$^-$, 523 (7) [M + Cl]$^-$, 545 (100) [M + CH_3COO]$^-$, 1029 (14) [2M + CH_3COO]$^-$. IR (KBr): ν = 1539, 1558, 1624 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2208, 2223 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{14}Cl_2N_4O_4Zn{\cdot}H_2O$: C, 42.84; H, 3.20; N, 11.10; found: C, 43.04; H, 3.13; N, 11.14. ICP-AES: anal. calcd. for $C_{18}H_{14}Cl_2N_4O_4Zn$: Zn, 13.44; found: Zn, 14.77. UV/Vis (MeCN): λ_{max} (ε) = 219 (21 180), 234 (shoulder; ~16 080), 317 (44 040), 376 (35 990) nm (mol^{-1} dm^3 cm^{-1}).

Zn[2b]. Procedure Zn-a with ligand **2b** (750 mg, 1.45 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.5 ml, 1.50 mmol). Yield: dark green solid (0.81 g, 1.40 mmol, 96%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.10 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 4.24 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.54 (s, 2H, CH_{aromat}), 8.80 (s, 2H, CH). $^{13}C\{^1H\}$ NMR (100 MHz, $SO(CD_3)_2$): δ = 14.21, 14.41 (CH_3), 58.79, 60.17 (CH_2), 89.23 (=C_q), 115.95 (CH_{aromat}), 125.53 ($C_{q,aromat}$–Cl), 139.73 ($C_{q,aromat}$), 158.86 (CH), 166.77, 171.18 (C=O). MS (ESI+) *m*/*z* (%): 425 (52) [M − 2OEt]$^+$, 471 (72) [Lig − OEt]$^+$, 517 (29) [Lig + H]$^+$, 539 (99) [Lig + Na]$^+$, 581 (100) [M + H]$^+$, 1161 (22) [2M + H]$^+$. MS (ESI−) *m*/*z* (%): 515 (6) [Lig − H]$^-$, 639 (100) [M + CH_3COO]$^-$, 1219 (21) [2M + CH_3COO]$^-$. IR (KBr): ν = 1527, 1576, 1603, 1677 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{24}Cl_2N_2O_8Zn$: C, 45.50; H, 4.17; N, 4.82; found: C, 45.23; H, 4.34; N, 4.71. ICP-AES: anal. calcd. for $C_{22}H_{24}Cl_2N_2O_8Zn$: Zn, 11.26; found: Zn, 11.17. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 253 (shoulder, ~13 390), 294 (21 190), 313 (25 490), 371 (22 930) nm (mol^{-1} dm^3 cm^{-1}).

Zn[2d]. Procedure Zn-a with ligand **2d** (500 mg, 1.06 mmol), THF (10 ml) and diethylzinc in hexane (1 M) (1.1 ml, 1.06 mmol). Yield: yellow solid (0.58 g, 0.88 mmol, 83%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.10 (q, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 4.24 (m, 4H, CH_2), 7.51 (s, 1H, CH_{aromat}), 7.90 (s, 1H, CH_{aromat}), 8.46 (s, 1H, CH), 8.77 (s, 1H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.22, 14.30, 14.41 (CH_3), 58.79, 60.10, 60.70 (CH_2), 69.45 (=C_q), 89.30 (=C_q), 115.91 (CH_{aromat}), 117.00 (CH_{aromat}), 120.92 (C≡N), 125.46 ($C_{q,aromat}$–Cl), 126.12 ($C_{q,aromat}$–Cl), 138.51 ($C_{q,aromat}$), 139.79 ($C_{q,aromat}$), 157.90 (CH), 158.69 (CH), 166.89, 170.88, 171.00 (C=O). MS (ESI−) *m*/*z* (%): 592 (100) [M + CH_3COO]$^-$, 1127 (32) [2M + CH_3COO]$^-$. IR (KBr): ν = 1558, 1602, 1635 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2233 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{19}Cl_2N_3O_6Zn{\cdot}3/2H_2O$: C, 42.84; H, 3.95; N, 7.49; found: C, 43.08; H, 3.94; N, 7.24. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 315 (9645), 375 (8324) nm (mol^{-1} dm^3 cm^{-1}).

Zn[3a]. Procedure Zn-b with ligand **3a** (750 mg, 1.96 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.9 ml, 1.90 mmol). Yield: yellow solid (0.61 g, 1.38 mmol, 70%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 2.18 (s, 6H, C_{aromat}–CH_3), 4.23 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.39 (s, 2H, CH_{aromat}), 8.32 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 M Hz, $SO(CD_3)_2$): δ = 14.36 (CH_3), 19.09 (C_{aromat}–CH_3), 60.33 (CH_2), 67.67 (=C_q), 115.84 (CH_{aromat}), 121.61 (C≡N), 132.82 ($C_{q,aromat}$–CH_3), 135.75 ($C_{q,aromat}$), 155.55 (CH), 170.96 (C=O). MS (ESI+) *m*/*z* (%): 337 (89) [Lig − OEt]$^+$, 383 (58) [Lig + H]$^+$, 400 (33) [Lig + NH_4]$^+$, 405 (93) [Lig − H]$^+$, 445 (100) [M + H]$^+$, 467 (5) [M + MeOH]$^+$, 787 (42) [2Lig + Na]$^+$, 889 (7) [2M + H]$^+$. MS (ESI−) *m*/*z* (%): 381 (14) [Lig − H]$^-$, 503 (100) [M + CH_3COO]$^-$, 947 (29) [2M + CH_3COO]$^-$. IR (KBr): ν = 1551, 1624 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2202, 2220 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{20}N_4O_4Zn$: C, 53.89; H, 4.52; N, 12.57; found: C, 53.63; H, 4.70; N, 12.64. ICP-AES: anal. calcd. for $C_{20}H_{20}N_4O_4Zn$: Zn, 14.67; found: Zn, 14.56. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 241 (15 820), 310 (25 630), 365 (21 270) nm (mol^{-1} dm^3 cm^{-1}).

Zn[3b]. Procedure Zn-a with ligand **3b** (750 mg, 1.55 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.6 ml, 1.60 mmol). Yield: brown solid (0.81 g, 1.49 mmol, 96%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 2.22 (s, 4H, C_{aromat}–CH_3), 4.09 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.23 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.14 (s, 2H, CH_{aromat}), 8.88 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.25, 14.41 (CH_3), 19.22 (C_{aromat}–CH_3), 58.51, 59.85 (CH_2), 87.32 (=C_q), 115.25 (CH_{aromat}), 132.34 ($C_{q,aromat}$–CH_3), 136.96 ($C_{q,aromat}$), 157.79 (CH), 166.99, 171.27 (C=O). MS (ESI+) *m*/*z* (%): 431 (100) [Lig − OEt]$^+$, 477 (35) [Lig + H]$^+$, 499 (34) [Lig + Na]$^+$, 539 (8) [M + H]$^+$, 975 (20) [2Lig + Na]$^+$. MS (ESI−) *m*/*z* (%): 475 (38) [Lig − H]$^-$, 597 (100) [M + CH_3COO]$^-$, 1139 (10) [2M + CH_3COO]$^-$. IR (KBr): ν = 1526, 1593, 1615, 1674 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{24}H_{30}N_2O_8Zn$: C, 53.39; H, 5.60; N, 5.19; found: C, 53.27; H, 5.95; N, 5.12. ICP-AES: anal. calcd. for $C_{24}H_{30}N_2O_8Zn$: Zn, 12.11; found: Zn, 11.35. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 292 (27 320), 335 (22 970) nm (mol^{-1} dm^3 cm^{-1}).

Zn[3d]. Procedure Zn-a with ligand **3d** (0.54 g, 1.35 mmol), THF (10 ml) and diethylzinc in hexane (1 M) (1.4 ml, 1.35 mmol). Yield: orange solid (0.63 g, 1.28 mmol, 95%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.29 (t, $^3J_{HH}$ = 6.3 Hz, 6H, CH_2), 2.19 (s, 3H, C_{aromat}–CH_3), 2.21 (s, 3H, C_{aromat}–CH_3), 4.09 (q, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 4.24 (m, 4H, CH_2), 7.12 (s, 1H, CH_{aromat}), 7.42 (s, 1H, CH_{aromat}), 8.36 (s, 1H, CH), 8.86 (s, 1H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.27, 14.35, 14.45 (CH_3), 19.10 (C_{aromat}–CH_3), 19.27 (C_{aromat}–CH_3), 58.54, 59.84, 60.45 (CH_2), 67.68 (=C_q), 87.40 (=C_q), 115.13 (CH_{aromat}), 116.00 (CH_{aromat}), 121.41 (C≡N), 132.24 ($C_{q,aromat}$–CH_3), 132.96 ($C_{q,aromat}$–CH_3), 135.80 ($C_{q,aromat}$), 136.91 ($C_{q,aromat}$), 155.84 (CH), 157.71 (CH), 167.09 (C=O), 171.19 (C=O). MS (ESI+) *m*/*z* (%): 430 (100) [Lig + H]$^+$, 452 (22) [Lig + Na]$^+$, 492 (18) [M + H]$^+$, 882 (13) [2Lig + Na]$^+$. MS (ESI−) *m*/*z* (%): 428 (21) [Lig − H]$^-$, 550 (100) [M + CH_3OO]$^-$, 1041 (21) [2M + CH_3COO]$^-$. IR (KBr): ν = 1547, 1600 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2202 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{22}H_{25}N_3O_6Zn{\cdot}2OH$: C, 50.15; H, 5.17; N, 7.98; found: C, 50.40; H, 5.17; N, 8.11. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 245 (9521), 310 (20 970), 367 (18 680) nm (mol^{-1} dm^3 cm^{-1}).

Zn[4a]. Procedure Zn-b with ligand **4a** (750 mg, 2.45 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.5 ml, 2.45 mmol). Yield: white solid (0.76 g, 2.04 mmol, 83%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1Hz, 6H, CH_3), 3.42 (s, 4H, CH_2–CH_2), 4.15 (q, $^3J_{HH}$ = 7.1Hz, 4H, CH_3), 7.82 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.40 (CH_3), 54.05 (CH_2), 59.58, 59.84 (CH_2–CH_2), 64.18 (=C_q), 121.85 (C≡N), 162.66 (CH), 171.77 (C=O). MS (ESI+) *m*/*z* (%): 307 (64) $[Lig + H]^+$, 324 (39) $[Lig + H_2O]^+$, 329 (80) $[Lig + Na]^+$, 345 (36) $[Lig + K]^+$, 369 (4) $[M + H]^+$, 635 (100) $[2Lig + Na]^+$. MS (ESI−) *m*/*z* (%): 305 (100) $[Lig - H]^-$, 368 (5) $[M - H]^-$, 673 (9) $[M + Lig]^-$. HR-MS (ESI+) *m*/*z*: anal. calcd. for $C_{14}H_{17}N_4O_4Zn$: 369.05358; found: 369.05401. IR (KBr): ν = 1528, 1562, 1649 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2206 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{14}H_{16}N_4O_4Zn$: C, 45.49; H, 4.36; N, 15.16; found: C, 45.04; H, 4.57; N, 15.07. ICP-AES: anal. calcd. for $C_{14}H_{16}N_4O_4Zn$: Zn, 17.69; found: Zn, 17.09.

Zn[4b]. Procedure Zn-a with ligand **4b** (1.00 g, 2.50 mmol), THF (20 ml) and diethylzinc in hexane (1 M) (2.5 ml, 2.50 mmol). Yield: white solid (0.8038 g, 1.73 mmol, 69%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.17 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 3.45 (s, 4H, CH_2–CH_2), 3.99 (d, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 4.13 (d, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 8.42 (s, 2H). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.70, 14.84 (CH_3), 55.53 (CH_2–CH_2), 58.35, 59.70 (CH_2), 84.50 (=C_q), 165.60 (CH), 168.04, 173.93 (C=O). MS (ESI−) *m*/*z* (%): 399 (100) $[Lig - H]^-$, 521 (16) $[M + CH_3COO]^-$, 861 (4) $[M + Lig - H]^-$. IR (KBr): ν = 1596, 1634, 1678 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{26}N_2O_8Zn{\cdot}H_2O$: C, 44.87; H, 5.86; N, 5.81; found: C, 44.65; H, 5.98; N, 5.83. ICP-AES: anal. calcd. for $C_{18}H_{26}N_2O_8Zn$: Zn, 14.10, found: Zn, 14.58.

Zn[5a]. Procedure Zn-b with ligand **5a** (750 mg, 2.34 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.3 ml, 2.30 mmol). Yield: white solid (0.64 g, 1.66 mmol, 71%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.70 (m, 2H, CH_2–CH_2), 3.53 (m, 4H, CH_2–N), 4.15 (t, $^3J_{HH}$ = 7.1 Hz, 4H, CH_3), 7.63 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.53 (CH_3), 31.05 (CH_2–CH_2), 59.79 (CH_3), 60.60 (CH_2–N), 63.25 (=C_q), 121.78 (C≡N), 163.96 (CH), 171.21 (C=O). MS (ESI−) *m*/*z* (%): 319 (100) $[Lig - H]^-$, 355 (2) $[Lig + Cl]^-$, 382 (5) $[M - H]^-$. IR (KBr): ν = 1562, 1637, 1683 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2194, 2211 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{15}H_{18}N_4O_4Zn{\cdot}H_2O$: C, 44.85; H, 5.02; N, 13.95; found: C, 44.64; H, 5.02; N, 14.08. ICP-AES: anal. calcd. for $C_{15}H_{18}N_4O_4Zn$: Zn, 17.04; found: Zn, 17.86.

Zn[5b]. Procedure Zn-a with ligand **5b** (750 mg, 1.81 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.8 ml, 1.80 mmol). Yield: white solid (0.80 g, 1.68 mmol, 93%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.16 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.23 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.74 (m, 2H, CH_2–CH_2), 3.54 (m, 4H, CH_2–N), 3.99 (q, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2), 4.14 (q, $^3J_{HH}$ = 7.1 Hz, 6H, CH_2), 8.25 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.51 (CH_3), 31.74 (CH_2–CH_2), 57.90, 59.05 (CH_2), 61.35 (CH_2–N), 82.93 (=C_q), 166.41 (CH), 166.57, 171.02 (C=O). MS (ESI−) *m*/*z* (%): 367 (9) $[Lig - OEt]^-$, 413 (100) $[Lig - H]^-$, 511 (4) $[M + Cl]^-$. IR (KBr): ν = 1603, 1659, 1696 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{19}H_{28}N_2O_8Zn{\cdot}2H_2O$: C, 44.41; H, 6.28; N, 5.45; found: C, 44.03; H, 6.37; N, 5.38. ICP-AES: anal. calcd. for $C_{19}H_{28}N_2O_8Zn$: Zn, 13.68; found: Zn, 14.71.

Zn[6a]. Procedure Zn-b with ligand **6a** (750 mg, 2.24 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.2 ml, 2.20 mmol). Yield: white solid (0.56 g, 1.40 mmol, 62%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 1.68 (s, 4H, CH_2–CH_2), 3.35 (m, 4H, CH_2–N), 4.14 (q, $^3J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.72 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.856 (CH_3), 27.677 (CH_2–CH_2), 48.833 (CH_2–N), 59.97 (CH_3), 69.257 (=C_q), 117.364 (C≡N), 165.068 (CH), 171.644 (C=O). MS (ESI+) *m*/*z* (%): 243 (64) $[Lig - 2OEt]^+$, 289 (100) $[Lig - OEt]^+$, 307 (70) $[Lig - OEt + NH_4]^+$, 335 (44) $[Lig + H]^+$, 357 (100) $[Lig + Na]^+$, 397 (8) $[M + H]^+$, 691 (15) $[2Lig + Na]^+$. MS (ESI−) *m*/*z* (%): 333 (100) $[Lig - H]^-$, 351 (3) $[M - OEt]^-$, 396 (6) $[M - H]^-$, 455 (4) $[M + CH_3COO]^-$, 729 (4) $[M + Lig - H]^-$. IR (KBr): ν = 1463, 1623, 1678 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2210 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{16}H_{20}N_4O_4Zn{\cdot}2OH$: C, 44.51; H, 5.14; N, 12.98; found: C, 44.81; H, 5.50; N, 13.29. ICP-AES: anal. calcd. for $C_{16}H_{20}N_4O_4Zn$: Zn, 16.44; found: Zn, 16.43.

Zn[6b]. Procedure Zn-a with ligand **6b** (750 mg, 1.75 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (1.8 ml, 1.80 mmol). Yield: white solid (0.85 g, 1.64 mmol, 94%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.19 (m, 12H, CH_3), 1.71 (s, 4H, CH_2–CH_2), 3.35 (s, 4H, CH_2–N), 4.05 (m, 8H, CH_2), 8.33 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.22, 14.28 (CH_3), 27.245 (CH_2–CH_2), 48.447 (CH_2–N), 58.63, 59.12 (CH_2), 87.854 (=C_q), 159.381 (CH), 166.67, 167.70 (C=O). MS (ESI+) *m*/*z* (%): 337 (84) $[Lig - 2OEt]^+$, 355 (5) $[Lig - 2OEt + NH_4]^+$, 369 (16) $[Lig - 2OEt + MeOH]^+$, 383 (100) $[Lig - OEt]^+$, 429 (5) $[Lig + H]^+$, 451 (59) $[Lig + Na]^+$, 491 (3) $[M + H]^+$. IR (KBr): ν = 1629, 1679 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for $C_{20}H_{30}N_2O_8Zn{\cdot}H_2O$: C, 47.02; H, 6.51; N, 5.48; found: C, 47.07; H, 6.85; N, 5.47. ICP-AES: anal. calcd. for $C_{20}H_{30}N_2O_8Zn$: Zn, 13.29; found: Zn, 14.25.

Zn[7a]. Procedure Zn-b with ligand **7a** (750 mg, 2.08 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.1 ml, 2.10 mmol). Yield: white solid (0.78 g, 1.85 mmol, 89%). ^{1}H-NMR (400 MHz, $SO(CD_3)_2$): δ = 1.24 (m, 10H, CH_3, $CH_{2,cyclo}$), 1.80 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $CH_{2,cyclo}$), 2.25 (d, $^3J_{HH}$ = 11.8 Hz, 2H, $CH_{2,cyclo}$), 2.83 (d, $^3J_{HH}$ = 8.7 Hz, 2H, CH_{cyclo}), 4.16 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 7.69 (s, 2H, CH). $^{13}C\{^1H\}$-NMR (100 MHz, $SO(CD_3)_2$): δ = 14.395 (CH_3), 23.903 ($CH_{2,cyclo}$), 27.482 ($CH_{2,cyclo}$), 59.916 (CH_3), 64.123 (CH_{cyclo}), 121.996 (=C_q), 158.983 (CH), 171.716 (C=O). MS (ESI+) *m*/*z* (%): 269 (45) $[Lig - 2OEt]^+$, 289 (40) $[Lig - 2OEt + NH_4]^+$, 315 (100) $[Lig - OEt]^+$, 333 (45) $[Lig - OEt + NH_4]^+$, 361 (81) $[Lig + H]^+$, 378 (52) $[Lig + NH_4]^+$, 383 (44) $[Lig + Na]^+$, 423 (5) $[M + H]^+$, 743 (20) $[2 Lig + Na]^+$. IR (KBr): ν = 1563, 1639, 1680 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2201, 2213 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for $C_{18}H_{22}N_4O_4Zn{\cdot}1/2OH$: C, 50.01; H, 5.25; N, 12.96; found: C, 50.20; H, 5.40; N, 13.09. ICP-AES: anal. calcd. for $C_{18}H_{22}N_4O_4Zn$: Zn, 15.43; found: Zn, 15.15.

Zn[7b]. Procedure Zn-a with ligand **7b** (5.00 g, 1.10 mmol), THF (10 ml) and diethylzinc in hexane (1 M) (1.1 ml, 1.10 mmol). Yield: yellowish solid (0.57 g, 1.11 mmol, >99%).

^{1}H-NMR (400 MHz, SO(CD$_3$)$_2$): δ = 1.20 (m, 14H, CH$_3$, CH$_{2,cyclo}$), 1.33 (m, 2H, CH$_{2,cyclo}$), 1.84 (d, $^3J_{HH}$ = 5.7 Hz, 2H, CH$_{2,cyclo}$), 2.17 (d, $^3J_{HH}$ = 10.8 Hz, 2H, CH$_{2,cyclo}$), 2.85 (d, $^3J_{HH}$ = 6.5 Hz, 2H, CH$_{cyclo}$), 4.00 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH$_2$), 4.14 (m, 4H, CH$_2$), 8.39 (s, 2H, CH). ^{13}C{^{1}H}-NMR (100 MHz, SO(CD$_3$)$_2$): δ = 14.16 (CH$_3$), 23.94 (CH$_{2,cyclo}$), 31.48 (CH$_{2,cyclo}$), 58.48, 58.65 (CH$_2$), 62.60 (CH$_{2,cyclo}$), 88.20 (=C$_q$), 158.82 (CH), 164.83, 167.69 (C=O). MS (ESI+) *m*/*z* (%): 455 (27) [Lig + H]$^+$, 477 (88) [Lig + Na]$^+$, 517 (7) [M + H]$^+$, 539 (17) [M + Na]$^+$, 930 (100) [2Lig + Na]$^+$. IR (KBr): ν = 1592, 1654, 1676, 1713 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for C$_{22}$H$_{32}$N$_2$O$_8$Zn·H$_2$O·OH: C, 47.79; H, 6.38; N, 5.07; found: C, 48.07; H, 6.56; N, 5.05. ICP-AES: anal. calcd. for C$_{22}$H$_{32}$N$_2$O$_8$Zn: Zn, 12.62; found: Zn, 12.66.

Zn[8a]. Procedure Zn-a with ligand **8a** (750 mg, 2.04 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.0 ml, 2.00 mmol). Yield: white solid (0.26 g, 0.60 mmol, 29%). ^{1}H-NMR (400 MHz, SO(CD$_3$)$_2$): δ = 1.24 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 4.16 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH$_2$), 4.24 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH$_2$), 4.46 (s, 2H, CH$_2$–N), 7.11 (m, 2H, CH$_{aromat}$), 7.24 (dd, $^3J_{HH}$ = 1.3 Hz, $^4J_{HH}$ = 7.6 Hz, 1H, CH$_{aromat}$), 7.32 (dt, $^3J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 7.7 Hz, 1H, CH$_{aromat}$), 7.87 (s, 1H, CH), 7.91 (s, 1H, CH). ^{13}C{^{1}H}-NMR (100 MHz, SO(CD$_3$)$_2$): δ = 14.35, 14.42 (CH$_3$), 59.97 (CH$_2$), 60.68 (CH$_2$), 61.47 (CH$_2$–N), 63.88 (=C$_q$), 68.37 (=C$_q$), 120.52 (CH$_{aromat}$), 120.97 (C≡N), 121.60 (C≡N), 124.61 (CH$_{aromat}$), 129.03, 129.13 (CH$_{aromat}$), 131.10 (C$_{q,aromat}$), 149.00 (C$_{q,aromat}$), 161.56 (CH), 164.04 (CH), 171.18 (C=O), 171.72 (C=O). MS (ESI+) *m*/*z* (%): 369 (100) [Lig + H]$^+$, 386 (62) [Lig + NH$_4$]$^+$, 391 (98) [Lig + Na]$^+$, 431 (10) [M + H]$^+$, 453 (3) [M + Na]$^+$. MS (ESI−) *m*/*z* (%): 367 (100) [Lig − H]$^-$, 489 (34) [M + CH$_3$COO]$^-$, 797 (9) [M + Lig − H]$^-$. HR-MS (ESI+) *m*/*z*: anal. calcd. for C$_{19}$H$_{19}$N$_4$O$_4$Zn: 431.06923; found: 431.06960. IR (KBr): ν = 1553, 1628 (s, $\nu_{C=O}$; $\nu_{C=N}$), 2202 (s, $\nu_{C\equiv N}$) cm^{-1}. Anal. calcd. for C$_{19}$H$_{18}$N$_4$O$_4$Zn: C, 52.86; H, 4.20; N, 12.98; found: C, 52.17; H, 4.33; N, 12.83. ICP-AES: anal. calcd. for C$_{19}$H$_{18}$N$_4$O$_4$Zn: Zn, 15.14; found: Zn, 15.61. UV/Vis (MeCN): λ_{max} (ε) = 220 (30 290), 297 (35 960), 327 (21 240) nm (mol^{-1} dm^3 cm^{-1}).

Zn[8b]. Procedure Zn-a with ligand **8b** (1.00 g, 2.16 mmol), THF (15 ml) and diethylzinc in hexane (1 M) (2.2 ml, 2.20 mmol). Yield: beige solid (1.08 g, 2.05 mmol, 95%). ^{1}H-NMR (400 MHz, SO(CD$_3$)$_2$): δ = 1.19, 1.20, 1.24, 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH$_3$), 4.02, 4.06, 4.14, 4.22 (q, $^3J_{HH}$ = 7.1 Hz, 8H, CH$_2$), 4.47 (s, 2H, CH$_2$–N), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 1H, CH$_{aromat}$), 7.09 (dt, $^3J_{HH}$ = 1.0 Hz, $^4J_{HH}$ = 7.4 Hz, 1H, CH$_{aromat}$), 7.33 (m, 2H, CH$_{aromat}$), 8.49 (s, 2H, CH). ^{13}C{^{1}H}-NMR (100 MHz, SO(CD$_3$)$_2$): δ = 14.34, 14.35, 14.41, 14.54 (CH$_3$), 58.05, 58.44, 59.31, 59.93 (CH$_2$), 62.70 (CH$_2$–N), 83.68, 87.54 (=C$_q$), 120.15 (CH$_{aromat}$), 124.15 (CH$_{aromat}$), 129.09, 129.14 (CH$_{aromat}$), 131.63 (CH$_{q,aromat}$), 150.12 (CH$_{q,aromat}$), 163.59 (CH), 166.29 (CH), 166.53, 171.12 (C=O). MS (ESI+) *m*/*z* (%): 415 (7) [Lig − OEt − H]$^-$, 461 (100) [Lig − H]$^-$, 507 (5) [Lig + HCOO]$^-$, 583 (9) [M + CH$_3$COO]$^-$. IR (KBr): ν = 1589, 1616, 1641, 1664, 1694, 1706 (s, $\nu_{C=O}$; $\nu_{C=N}$) cm^{-1}. Anal. calcd. for C$_{23}$H$_{28}$N$_2$O$_8$Zn·H$_2$O: C, 50.79; H, 5.56; N, 5.15; found: C, 50.99; H, 5.60; N, 5.23. ICP-AES: anal. calcd. for C$_{23}$H$_{28}$N$_2$O$_8$Zn: Zn, 12.43; found: Zn, 12.31.

Procedure of the catalytic screening tests

The efficiency of the zinc catalysts was tested in a "test bench" consisting of eight 70 ml autoclaves (material 1.4571-stainless austenitic steel-316Ti, 70 ml, P_{max} 200 bar, T_{max} 250 °C) equipped with multimeters (Agilent 34970A Data Acquisition/Data Logger Switch Unit + 34901A 20 Channel Multiplexer) and PCs for *p*-,*T*-acquisition and aluminum blocks for external heating. The selected catalyst and the cocatalyst were loaded in an autoclave that was afterwards heated under vacuum. After cooling, the autoclave was purged with argon and the epoxide (10 ml, 0.143 mol) was injected *via* a port of the autoclave. Afterwards, the autoclave was loaded with a definite quantity of CO_2 (weighted) and the reaction started (heating). After a reaction time of 20 h the autoclaves were cooled down to room temperature and excess CO_2 was removed by venting slowly the autoclaves under a fume hood. The reaction mixtures/products were collected from the autoclaves by dissolving them in dichloromethane, which was afterwards removed from the products in vacuum, like the traces of unreacted epoxide.

The experiments under a pressure of 2 bar were realized by connecting the autoclave to a CO_2-cylinder during the whole course of the reaction, the CO_2-line being equipped with a calibrated back pressure regulator. After adding the epoxide (10 ml, 0.143 mol) into the autoclave, it was connected to the CO_2-container and the autoclave was heated. After a short period of time, the pressure in the autoclave evens out at 2 bar.

After drying the product mixture under vacuum, it was analyzed by IR and NMR spectroscopy. IR spectroscopy was used to check the presence of cyclic carbonate by its characteristic C=O-vibrations at 1800 cm^{-1}.

After the NMR (in C_6D_6) revealed that the product contains pure cyclic carbonate, its yield was determined by weighing the dried product and subtracting the amount of catalyst and cocatalyst from the result (this method delivers more reliable results than the two-step method: distillation and weighing of the cyclic carbonate).

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