Supplementary Information

Mixed magnesium/zinc calix[4]arenes: Structure and ring opening polymerization capability.

Henry J. S. Banks,[a] Josef W.A. Frese,[a] Mark R. J. Elsegood,[a] and Carl Redshaw.[b]*

[a] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.*

[b] *Plastics Collaboratory, Chemistry, School of Natural Sciences, University of Hull, Cottingham Rd, Hull, HU6 7RX, UK*

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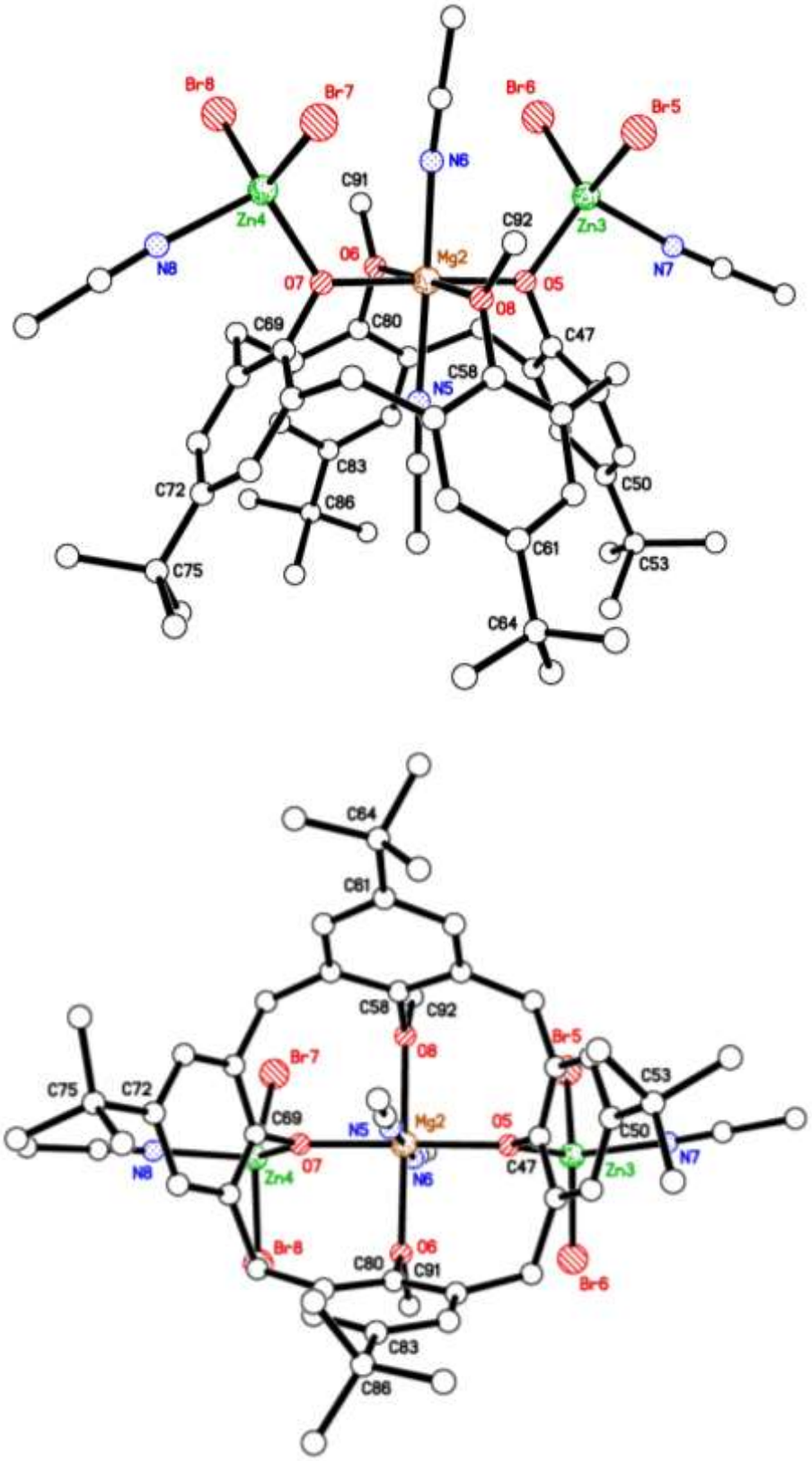


Figure S1. Two views of the molecular structure of the second molecule of **1**·1.5MeCN.

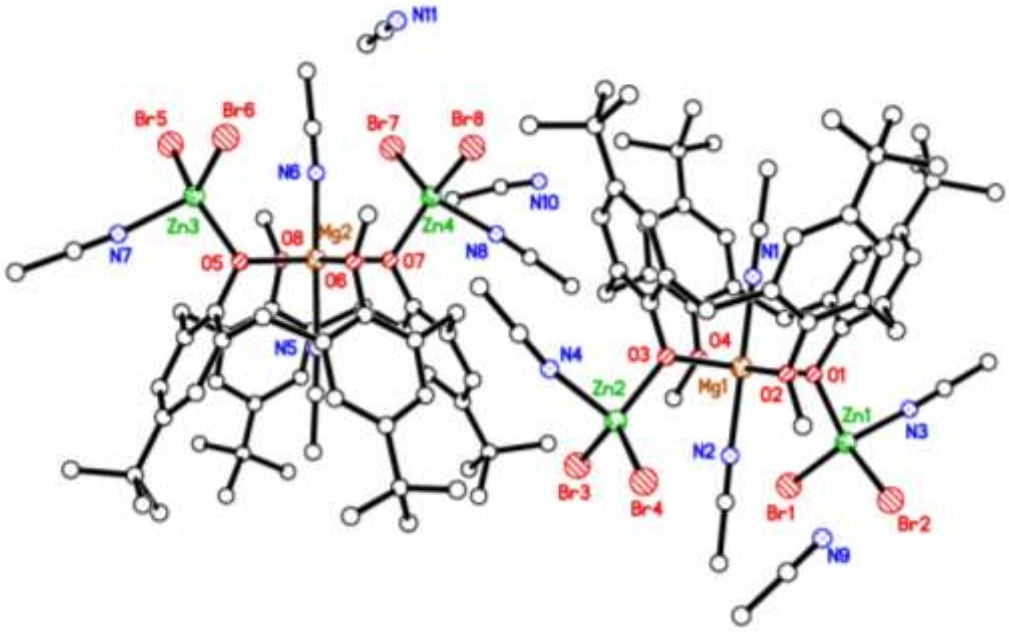


Figure S2. The asymmetric unit of **1**·1.5MeCN.

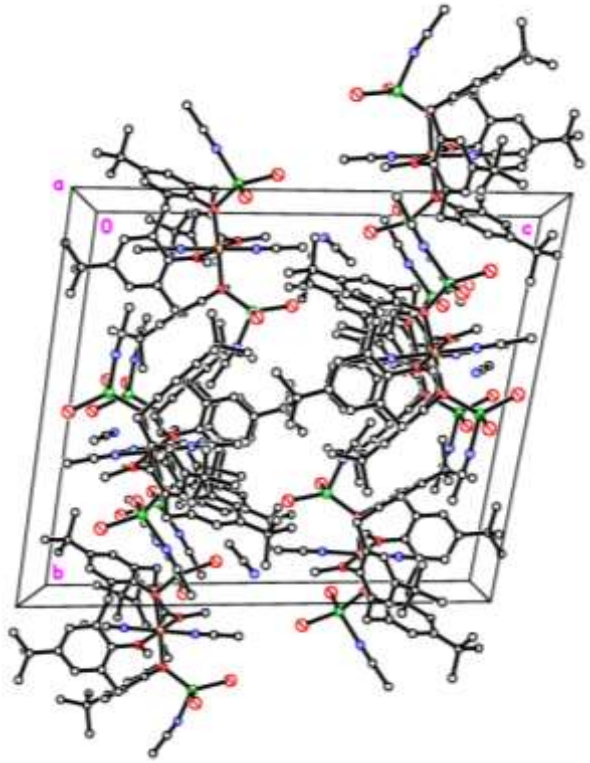


Figure S3. Packing of **1**·1.5MeCN.

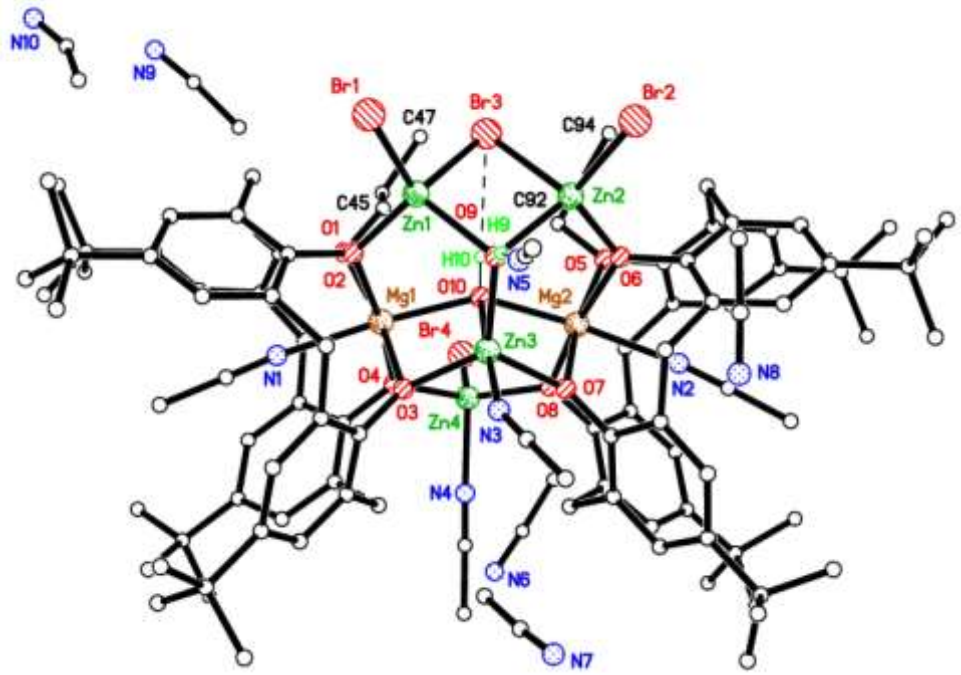


Figure S4. Alternative view of the molecular structure of **2**·5.19MeCN.

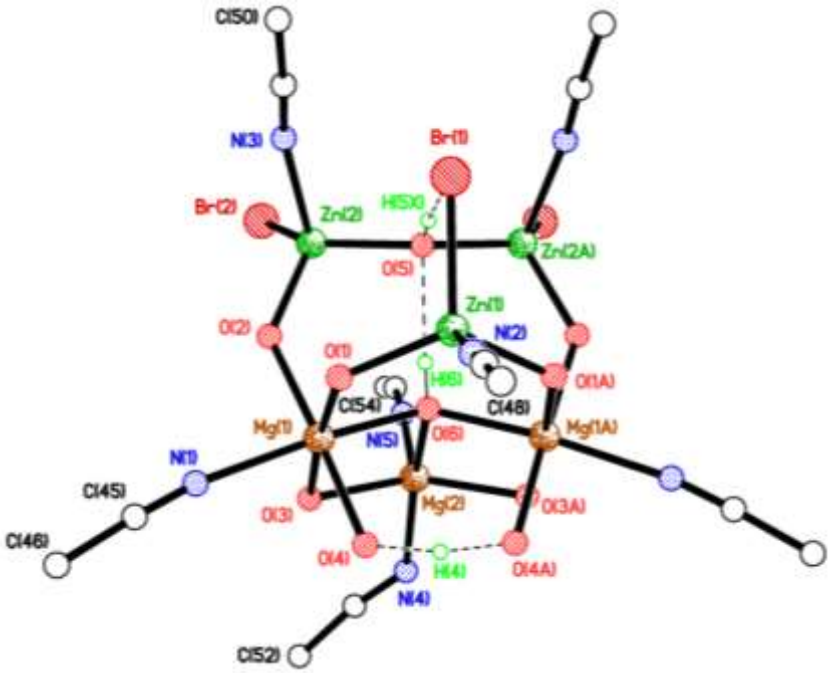


Figure S5. View of the core of **3**·4MeCN.

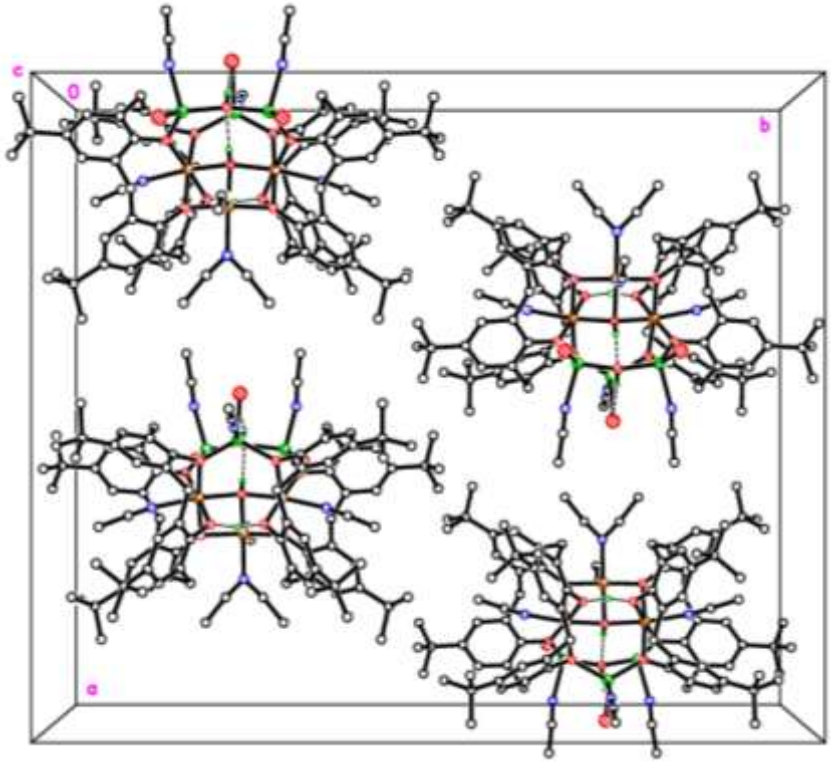
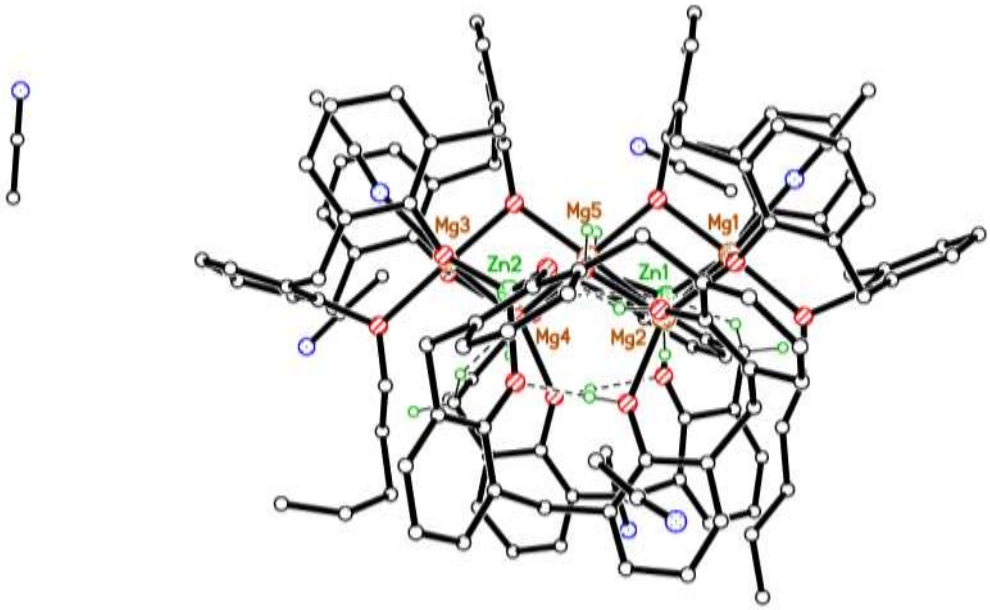


Figure S6. Packing in **3**·4MeCN.



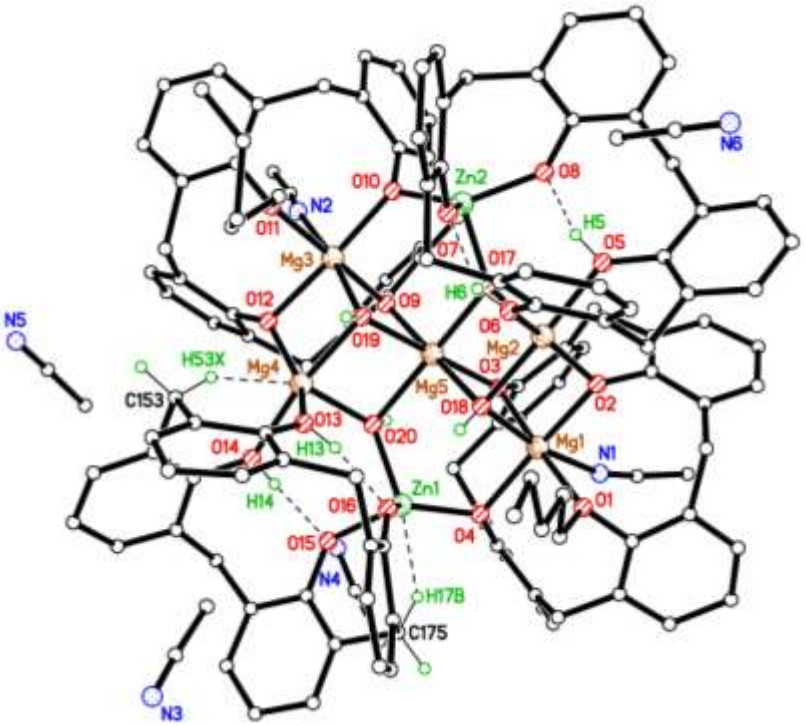


Figure S7. Two views of the molecular structure of **4**·5MeCN (*tert*-butyl groups removed for clarity).

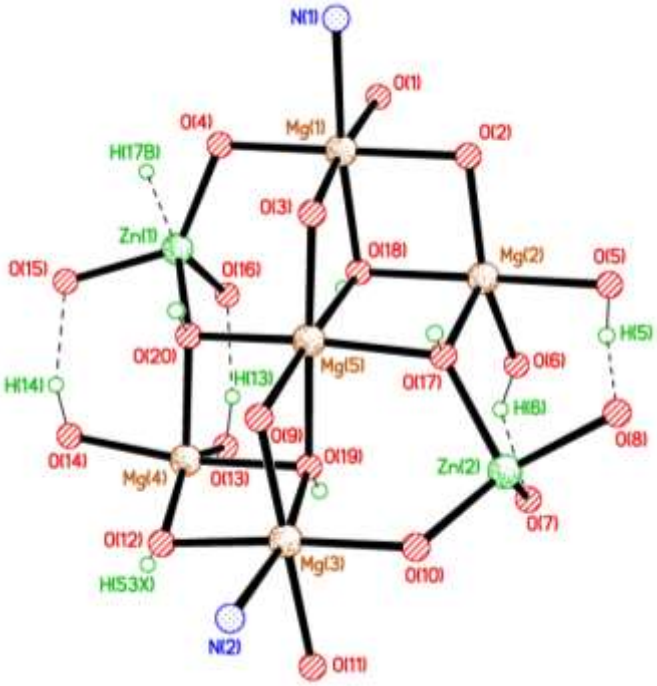


Figure S8. Core of **4**·5MeCN

Table S1. Crystallographic data for **1**·1.5(MeCN), **2**·5.19MeCN, **3**·4MeCN and **4**·5MeCN.

Compound	**1**·1.5(MeCN)	**2**·5.19MeCN
Formula	$C_{57}H_{74.5}Br_{2.94}Cl_{1.06}MgN_{5.5}O_4Zn_2$	$C_{112.37}H_{147.56}Br_{3.42}Cl_{0.58}Mg_2N_{9.19}O_{10}Zn_4$
Formula weight	1328.13	2390.84
Crystal system	Triclinic	Monoclinic
Space group	$P\ \bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	13.4199(15)	19.81378(8)
b (Å)	20.874(2)	25.56149(11)
c (Å)	23.345(3)	24.42596(10)
α (º)	96.6727(19)	90
β (º)	97.5170(19)	108.3869(4)
γ (º)	107.5764(19)	90
V (Å^3)	6096.2(12)	11739.44(9)
Z	4	4
Temperature (K)	150(2)	100(2)
Wavelength (Å)	0.71073	1.54178
Calculated density (g.cm^{-3})	1.447	1.353
Absorption coefficient (mm^{-1})	2.82	2.97
Transmission factors (min./max.)	0.219 and 0.702	0.463 and 1.000
Crystal size (mm^3)	0.63 × 0.14 × 0.11	0.19 × 0.09 × 0.02
ϑ(max) (°)	28.4	68.2
Reflections measured	101114	304295
Unique reflections	29963	21421

R_{int}	0.062	0.055
Reflections with $F^2 > 2\sigma(F^2)$	19044	19525
Number of parameters	1391	1487
R_1 [$F^2 > 2\sigma(F^2)$]	0.051	0.058
wR_2 (all data)	0.121	0.165
GOOF, S	1.03	1.08
Largest difference peak and hole (e Å^{-3})	1.19 and –0.70	1.89 and –1.86
Compound	**3**·4MeCN	**4**·5MeCN
Formula	$C_{108.92}H_{138.37}Br_{2.52}Cl_{0.48}Mg_3N_{10.46}O_{10}Zn_3$	$C_{200}H_{259}Mg_5N_7O_{20}Zn_2$
Formula weight	2241.34	3312.89
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma*	$P\ \bar{1}$
Unit cell dimensions		
a (Å)	28.44051(12)	17.1750(19)
b (Å)	33.62784(6)	23.5379(14)
c (Å)	12.56775(13)	25.6364(16)
α (º)	90	89.281(5)
β (º)	90	73.491(7)
γ (º)	90	87.287(7)
V (Å^3)	12019.71(14)	9925.5(14)
Z	4	2
Temperature (K)	100(2)	100(2)
Wavelength (Å)	1.54178	1.54178
Calculated density (g.cm^{-3})	1.239	1.115

Absorption coefficient (mm^{-1})	2.37	0.93
Transmission factors (min./max.)	0.761 and 1.000	0.693 and 1.000
Crystal size (mm^3)	0.24 × 0.22 × 0.14	0.36 × 0.12 × 0.01
ϑ(max) (°)	68.3	57.5
Reflections measured	186976	95866
Unique reflections	11175	26084
R_{int}	0.037	0.182
Reflections with $F^2 > 2\sigma(F^2)$	10629	12203
Number of parameters	723	2328
R_1 [$F^2 > 2\sigma(F^2)$]	0.072	0.245
wR_2 (all data)	0.205	0.685
GOOF, S	1.06	1.02
Largest difference peak and hole (e Å^{-3})	2.07 and –1.04	2.20 and –0.84

X-Ray Crystallography for 1·1.5(MeCN), **2**·5.19MeCN, **3**·4MeCN and **4**·5MeCN**.**

X-ray diffraction data were collected by the EPSRC National Crystallography Service using diffractometers equipped with rotating anode X-ray sources and HPAD detectors except for **1**·1.5MeCN which was collected using a conventional sealed tube X-ray source and a CCD detector. Crystals were cooled to 100 K during data collection (150 K for **1**·1.5MeCN). Data were integrated and corrected for absorption and Lp effects using standard methods. [S1] Structures were solved using dual-space methods within SHELXT [S2a] (direct methods within SHELXS for **1**·1.5MeCN [S2b]) and refined

against F^2 using least squares methods implemented within SHELXL. [S3] As with many calixarene complexes crystallised from MeCN, the exact amount of solvent of crystallization should be regarded as approximate. Further details are provided in Table S1 below, in the cifs deposited with the CCDC, and in the following section for structure-specific treatment of non-standard issues.

For **1**·1.5MeCN: The halogen sites were found to be a mixture of Br and Cl with refined occupancies: Br(1):Cl(1X) = 0.647:0.353(3); Br(2):Cl(2X) = 0.855:0.145(3); Br(3):Cl(3X) = 0.681:0.319(3); Br(4):Cl(4X) = 0.897:0.103(3); Br(5):Cl(5X) = 0.597:0.403(3); Br(6):Cl(6X) = 0.824:0.176(3); Br(7):Cl(7X) = 0.508:0.492(3); and Br(8):Cl(8X) = 0.864:0.136(3). Three MeCNs of crystallisation. In one of these, atoms N(11) and C(113) are modelled as split over 2 sets of positions with major occupancy 73.1(12)%

For **2**·5.19MeCN: As with **1**, three of the halogen sites were found to be a mixture of Br and Cl with refined occupancies: Br(1):Cl(1X) = 0.967:0.033(5); Br(2):Cl(2X) = 0.852:0.148(5); Br(3):Cl(3X) = 0.599:0.401(4). Br(4) was all bromine. There is linked two-fold disorder modelled in the two *n*Pr groups with the two terminal carbons and bonded H atoms split over two sets of positions. So, at C(45) and C(92) the major occupancy is 68.6(7)%. *t*Bu groups at C(29), C(41), C(54), and C(87) were also modelled as having the methyl groups two-fold disordered with major occupancies 77.8(10), 59.5(9), 80.3(9), and 60.1(10)% respectively. The MeCN of crystallisation including N(9) is only present when the major disorder component in the C(45)-containing *n*Pr group is present, so has occupancy 68.6(7)%. The MeCN of crystallisation at N(10) was modelled with 50% occupancy as it was either diffuse or partially present. In total there are *ca*. 5.19 MeCNs of crystallisation per complex.

For **3**·4MeCN: As with **1** and **2**, both of the halogen sites were found to be a mixture of Br and Cl with refined occupancies: Br(1):Cl(1X) = 0.826:0.174(6); Br(2):Cl(2X) = 0.845:0.155(6). Both of the MeCNs N(4) > C(52) and N(5) > C(54) coordinated with Mg(2) are 2-fold disordered. N(4) > C(52) is disordered due to N(4) lying on the plane of symmetry (50/50), whereas N(5) > C(54) can alter depending on the position of Zn(2) which is also disordered and here the major component is 52.0(17)%. Zn(2) is modelled as disordered and has been split between the positions Zn(2) and Zn(2X) with major component 72.9(2)%. In the case of Zn(2X) there is potential for an additional interaction with N(5X). O(5) is also modelled as disordered and has been split between O(5) and O(5X), with major component 75.7(10)%; H-bonding to Br(1) can occur when the oxygen occupies the O(5) position but not O(5X). Note O(6)–H(6) = 0.83(2) Å, O(6)···O(5) = 2.801 Å, but O(6)···O(5X) = 3.734 Å. Two of the 4 unique

*t*Bu groups on the calixarene are modelled as disordered but in separate ways. In the *t*Bu group containing C(29) the entire group is disordered whereas in the *t*Bu group containing C(40) the central carbon is fixed and the other carbons have rotated around this point. Major components are 78.5(9) and 85.8(8)%, respectively.

For **4**·5MeCN: The data set is very weak and subject to unresolved twinning, but the connectivity is remarkably well established considering the poor *R* factor, and it was sufficiently intriguing to merit inclusion in this paper. Me groups in *t*Bu calixarenes were modelled as two-fold disordered at C(7), C(18), C(78), C(111), C(122), and C(160) with major disorder components 53(3), 58(3), 56(3), 53(5), 65(3), and 65(2)%, respectively. *U* value restraints were used for all of these disordered groups and three MeCNs including N(1), N(6), & N(7). There are 5 MeCNs of crystallisation of which 0.5 was included via the Platon Squeeze procedure [S4]. MeCN at N(7) was refined at half-weight. MeCNs including N(3) & N(6) reside in calixarene cavities without pentyl groups. MeCNs containing N(1) & N(2) are coordinated to Mg ions within calixarene cavities with the pentyl groups. For the OH^- moieties, three had H atoms refined with distance restraints, the other with constraints {O(18)–H(18)}. Residual calixarene O*H* atoms were also refined with distance restraints.

CCDC 2298247-2298250 contain the supplementary crystallographic data for **1**·1.5(MeCN), **2**·5.19MeCN, **3**·4MeCN and **4**·5MeCN. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Experimental procedures

General

All reactions were conducted under an inert atmosphere using standard Schlenk techniques. Toluene was dried from sodium, acetonitrile was distilled from calcium hydride, THF was distilled from sodium benzophenone, and all solvents were degassed prior to use. IR spectra (nujol mulls, KBr or NaCl windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer; ^{1}H NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Advance DPX-300 spectrometer at 300 MHz. The ^{1}H NMR spectra were calibrated against the residual protio impurity of the deuterated solvent. Elemental analyses were performed by the elemental

analysis service at the University of Hull. Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrometry was performed in a Bruker autoflex III smart beam in linear mode, and the spectra were acquired by averaging at least 100 laser shots. 2,5-Dihydroxybenzoic acid was used as the matrix and THF as solvent. Sodium chloride was dissolved in methanol and used as the ionizing agent. Samples were prepared by mixing 20 μl of matrix solution in THF (2 mg·mL^{-1}) with 20 μL of matrix solution (10 mg·mL^{-1}) and 1 μL of a solution of ionizing agent (1 mg·mL^{-1}). Then 1 mL of these mixtures was deposited on a target plate and allowed to dry in air at ambient temperature. The calixarenes $L(OMe)_2H_2$, $L(O\textit{n}Pr)_3H$ and $L(O\textit{n}\text{-Pentyl})_3H$ were prepared using reported methods. [S5]

Preparation of $\{Mg(NCMe)_2[ZnX_2(NCMe)]_2L(OMe)_2\}\cdot 1.5MeCN$ (**1**·1.5MeCN) $\{X_2 = Br_{1.47}Cl_{0.53}\}$

To $L(OMe)_2H_2$ (1.00 g, 1.48 mmol) in THF (50 mL) at 0 ºC was added nonafluorobiphenylMgBr (1.48 mL, 1M, 1.48 mmol) and the system was allowed to warm to ambient temperature and stirred for 12 h. On cooling, the volatiles were removed and Br_2Zn (0.67 g, 3.0 mmol) and toluene (30 mL) were added and the system was refluxed for 12 h. On cooling, the volatiles were removed *in-vacuo*, and the residue was extracted into acetonitrile (20 mL). Cooling in the fridge afforded colourless crystals of **1**. Yield 0.89 g, 46%. $C_{54}H_{70}X_4MgN_4O_4Zn_2$ $\{X_4 = Br_{2.94}Cl_{1.06}\}$ (sample dried *in-vacuo* for 2h, –1.5MeCN) requires C 51.20, H 5.57, N 4.42%. Found C 49.92, H 5.67, N 4.91%. IR: 3448bm, 2726w, 2034bw, 1636bs, 1300m, 1260s, 1203s, 1170w, 1102s, 1016s, 975m, 936w, 874m, 801s, 722s. M.S. (MALDI-ToF): 1111 (M^+ –3MeCN –Br).

Preparation of $[(ZnBr(NCMe)][XZn(\mu\text{-}X)ZnX](\mu^3\text{-}OH)_2[Mg(MeCN)L(O\textit{n}\text{-}Pr)]_2\cdot 5.19MeCN$ (**2**·5.19MeCN) $\{3X = Br_{2.42}Cl_{0.58}\}$

To $L(O\textit{n}Pr)_3H$ (1.00 g, 1.29 mmol) in THF (30 mL) at 0 ºC was added $\textit{n}\text{-}Bu_2Mg$ (1.29 mL, 1M solution in heptane, 1.29 mmol) and the system was allowed to warm to room temperature and stirred for 12h. Br_2Zn (0.58 g, 2.6 mmol) was then added and the system was refluxed for 12h. On cooling, the volatiles were removed *in-vacuo*, and the residue was extracted into acetonitrile (20 mL). On standing at ambient temperature for 2 days, colourless blocks of **2**·5.31MeCN formed. Yield 1.18 g, 76%. $C_{102}H_{128}X_4Mg_2N_4O_{10}Zn_4\cdot 5.19MeCN$ $\{X_4 = Br_{3.42}Cl_{0.58}\}$ requires C

56.54, H 6.06, N 5.39%. Found C 54.95, H 5.81, N 5.23 %. IR: 3310bm, 2317w, 1599w, 1300s, 1261s, 1199s, 1123s, 1097s, 1062s, 1010s, 969s, 946m, 890w, 869s, 803s, 722s, 634w. M.S. (MALDI-ToF): 1214 (M^+ - L(O*n*Pr)), 1190 (M^+ - L(O*n*Pr) - Mg), 1045 (M^+ - L(O*n*Pr) – Mg – Br - Zn). ^{1}H NMR (C_6D_6) δ: 9.93 (s, 1H, O*H*), 9.77 (s, 1H, O*H*), 7.12 (partially obscured d, 2H, aryl*H*), 7.04 (d, *J* 2.4 Hz, 4H, aryl*H*), 6.96 (s, 4H, aryl*H*), 6.89 (s, 1H, aryl*H*), 6.88 (s, 1H, aryl*H*), 6.81 (s, 4H, aryl*H*), 4.45 (d, *J* 13.6 Hz, 4H, *endo*-CH_2), 4.39 (d, *J* 13.0 Hz, 4H, *endo*-CH_2), 3.67 (t, *J* 6.8 Hz, 4H, OCH_2CH$_2$CH$_3$), 3.30 (d, 4H, *J* = 13.0 Hz, *exo*-CH_2), 3.29 (d, 4H, *J* = 13.6 Hz, *exo*-CH_2), 1.83 (m, 4H, OCH$_2$CH_2CH$_3$), 1.42 (s, 3H, *Me*CN), 1.25 (s, 36H, C(CH_3)$_3$), 1.02 (2x overlapping t, 6H, OCH$_2$CH$_2$CH_3), 0.98 (s, 3H, *Me*CN), 0.89 (s, 18H, C(CH_3)$_3$), 0.83 (s, 18H, C(CH_3)$_3$), 0.75 (s, 3H, *Me*CN).

Preparation of {[ZnX(NCMe)]$_3$[Mg(MeCN)]$_2$[Mg(MeCN)$_2$](μ^3-OH)$_2$(L)(LH)}·4MeCN (**3**·4MeCN) {X = $Br_{0.84}Cl_{0.16}$}

To L(O*n*-Pr)$_3$(OH) (1.00 g, 1.29 mmol) in THF (30 mL) at 0^{o}C was added Mg(*n*-Bu)$_2$ (1.29 mL, 1M solution in heptane, 1.29 mmol) and the system was allowed to warm to ambient temperature and stirred for 12h. Volatiles were then removed *in-vacuo*, toluene (30 mL) was added, and following filtration, Br_2Zn (0.58 g, 2.6 mmol) was added. After refluxing for 12h, volatiles were removed *in-vacuo*, and the residue was extracted into MeCN (30 mL). On standing at ambient temperature for 2 days, colourless blocks of **3**·4MeCN formed. Yield 0.76 g, 77% (based on Mg). $C_{102}H_{128}X_3Mg_3N_7O_{10}Zn_3$·4MeCN {$X_3$ = $Br_{2.52}Cl_{48}$} requires C 58.36, H 6.23, N 6.81%. Found C 57.39, H 5.84, N 6.81%. IR: 3443bs, 3184bs, 1660bs, 1306s, 1260m, 1202w, 1102w, 890w, 872m, 817m, 782s, 727s. M.S. (MALDI-ToF): 1916 (M^+ - 5MeCN). ^{1}H NMR (C_6D_6) δ: 10.37 (s, 2H, O*H*), 9.82 (s, 1H, O*H*), 7.36 (bm, 1H, aryl*H*), 7.24 (bm, 1H, aryl*H*), 7.20 (bm, 1H, aryl*H*), 7.10 (d, 1H, aryl*H*), 7.03 (s, 1H, aryl*H*), 6.96 - 6.95 (overlapping bm + s, 10H, aryl*H*), 6.89 (s, 1H, aryl*H*), 4.52 (d, *J* = 14.0 Hz, 2H, *endo*-CH_2), 4.45 (d, *J* = 12.8 Hz, 2H, *endo*-CH_2), 4.33 (overlapping d, 2H, *endo*-CH_2), 3.74 (overlapping d, 2H, *exo*-CH_2) 3.37 (d, *J* = 12.8 Hz, 2H, *exo*-CH_2), 3.35 (d, *J* = 13.6 Hz, 2H, *exo*-CH_2), 3.30 (overlapping d, 2H, *exo*-CH_2), 1.40 (bs, 1.5H, *Me*CN), 1.31 (s, 9H, *Me*CN), 1.16 (bs, 6H, *Me*CN),1.09 (s, 54H, C(CH_3)$_3$), 1.05 (s, 18H, C(CH_3)$_3$), 0.97 (bs, 4.5H, *Me*CN), 0.91 (bs, 4.5H, *Me*CN), 0.86 (bs, 1.5H, *Me*CN), 0.54 (bs, 6H, *Me*CN).

Preparation of $[Mg_5Zn_2(OH)_4(LH_2)_2(L\text{-pent})_2(NCMe)_2]\cdot 5MeCN$ **4**·5MeCN

As for **3**, but using L(O*n*-Pentyl)$_3$(OH) (1.00 g, 1.16 mmol), Mg(*n*-Bu)$_2$ (1.16 mL, 1M in heptane, 1.16 mmol) and Br_2Zn (0.52 g, 2.3 mmol) affording **4**·4.5MeCN as colourless prisms. Yield: 0.59 g, 77% (based on Mg). $C_{190}H_{244}Mg_5N_2O_{20}Zn_2\cdot 5MeCN$ requires C 72.06, H 7.83, N 2.94%. Found C 71.47, H 7.53, N 2.41%. IR: 3170bw, 1649m, 1300s, 1260s, 1092s, 1020s, 872m, 802s, 722m, 675w, 607w. M.S. (MALDI-ToF): 2988 (M^+ - 2MeCN – Mg – 2OH), 2174 (M^+ - 2MeCN – Mg – 4OH – LH_4 – Zn_2). ^{1}H NMR (C_6D_6) δ: 10.36 (s, 4H, OH), 9.99 (s, 1H, OH), 9.85 (s, 3H, OH), 7.35 (bm, 2H, aryl*H*), 7.17 (d, *J* = 1.8 Hz, 3H, aryl*H*), 7.09 (d, *J* = 2.4 Hz, 5H, aryl*H*), 7.03 (s, 4H, aryl*H*), 6.94 (overlapping m + s, 13H, aryl*H*), 6.87 (s, 4H, aryl*H*), 6.73 (bm, 1H, aryl*H*), 5.42 (overlapping d, 2H, *endo*-CH_2), 5.14 (d, *J* 10.8 Hz, 1H, *endo*-CH_2), 4.92 (overlapping d, *J* = 11.6 Hz, 3H, *endo*-CH_2), 4.80 (overlapping d, 1H, *endo*-CH_2), 4.50 (overlapping m + d, doublet *J* = 13.6 Hz, 3H, *endo*-CH_2), 4.48 (d, *J* = 12.8 Hz, 2H, *endo*-CH_2), 4.33 (overlapping d, 4H, *endo*-CH_2), 3.95 (overlapping d, 1H, *exo*-CH_2), 3.85 (t, 4H, *J* = 6.8 Hz, OCH_2), 3.66 (overlapping d, 1H, *exo*-CH_2), 3.37 (d, *J* = 13.2 Hz, 2H, *exo*-CH_2), 3.34 – 3.28 (overlapping d + m, 8H, *exo*-CH_2), 1.98 (m, 4H, *J* = 6.8 Hz, CH_2), 1.53 (m, 4H, CH_2), 1.34 (m, 4H, *J* = 8.0 Hz, CH_2), 1.30 (s, 56H, C(CH_3)$_3$), 1.28 (bs, 3H, *Me*CN), 1.25 (bs, 3H, *Me*CN), 1.08 (s, 56H, C(CH_3)$_3$), 1.04 (t, 3H, *J* = 7.2 Hz, CH_3), 0,99 (t, 3H, *J* = 7.2 Hz, CH_3), 0.95 (s, 56H, C(CH_3)$_3$), 0.90 (s, 56H, C(CH_3)$_3$), 0.37 (s, 3H, *Me*CN), -0.20 (bs, 1.5H, *Me*CN).

Procedure for ROP of ε-caprolactone

A toluene solution of pre-catalyst (0.010 mmol, 1.0 mL toluene) were added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then monomer (2.5 mmol) along with 1.5 mL toluene was added to the solution. The reaction mixture was then placed into an oil/sand bath pre-heated at 130 °C (or the required temperature), and the solution was stirred for the prescribed time. The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried *in-vacuo*.

For ROP runs as melts, 0.01 mmol of pre-catalyst was weighed out in the dry box, and combined with the requisite amount of BnOH, and then connected to the Schlenk line and heated at 130 ^{o}C for 24h. Quenching and subsequent work-up as above.

Kinetic studies

The polymerizations were carried out at 130 °C in toluene (2 mL) using 0.010 mmol of complex. The molar ratio of monomer to initiator was fixed at 500:1, and at appropriate time intervals, 0.5 μL aliquots were removed (under N_2) and were quenched with wet $CDCl_3$. The percent conversion of monomer to polymer was determined using ^1H NMR spectroscopy.

ROP studies

Table S2. ROP of ε-CL using **1** – **4**.

Entry	Catalyst	[CL]:[Cat]:BnOH[a]	Time	T(°C)	Conversion	M_n[c]	$M_n calc$[d]	Đ [e]
1	**1**	500:1:2	24	130	82	16880	46900	1.60
2	**1**	500:1:0	24	130	14	-	-	-
3	**1**	500:1:2	24	20	0	-	-	-
4	**1**	500:1:2	72	130	86	82040/1330	49190	1.57/1.09
5*	**1**	500:1:2	24	130	100	23680/1970	57180	1.40/1.17
6	**1**	500:1:2	4	130	3	-	-	-
7	**2**	500:1:2	24	20	0	-	-	-
8	**2**	500:1:2	24	60	0	-	-	-
9	**2**	500:1:2	24	90	0	-	-	-
10	**2**	500:1:2	1	130	0	-	-	-
11	**2**	500:1:2	24	130	66	13460	37770	1.57
12	**2**	500:1:2	72	130	52	29400/1290	29780	1.42/1.10
13	**2**	500:1:5	24	130	42	15140/4380	24080	1.09/1.41
13	**2**	500:1:0	24	130	2	-	-	-
14	**2**	100:1:2	24	130	<1	-	-	-
15	**2**	1000:1:2	24	130	3	-	-	-
16*	**2**	500:1:2	24	130	25	-	-	-
17	**3**	500:1:2	24	20	0	-	-	-
18	**3**	500:1:2	24	130	67	30780	38340	2.11
19	**3**	500:1:0	24	130	15	-	-	-
20	**3**	500:1:2	72	130	51	34260/1380	29210	1.32/1.13
	3	500:1:6	24	130	7			
21*	**3**	500:1:2	24	130	100	7480/1980	57180	1.13/1.23
22	**4**	500:1:2	24	20	0	-	-	-
23	**4**	500:1:2	24	130	81	42080	46330	1.53
24	**4**	500:1:2	72	130	100	52720	57180	1.40
25	**4**	500:1:0	24	130	6	-	-	-
	4	500:1:7	24	130	0	-	-	-
26*	**4**	500:1:2	24	130	4	-	-	-
27	**I**[f]	500:1:1	24	130	6	-	-	-
28*	**I**[f]	500:1:1	24	130	0	-	-	-
29	**II**[f]	500:1:2	24	90	>99	29765	56600	2.25
30	**II**[f]	500:1:0	24	90	57	19070	32550	2.10
31*	**L(OMe)H$_2$**	500:1:0	24	130	0	-	-	-

32*	**L(OPentyl)$_2$H$_2$**	500:1:0	24	130	1	-	-	-

[a] Reaction conducted in toluene; [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC analysis calibrated with polystyrene standards and multiplied by correction factor of 0.56. [d] F.W.[M]/[BnOH])(conversion)+BnOH. [e] Polydispersity index (M_w/M_n) were determined by GPC.[f] See Fig. S9.

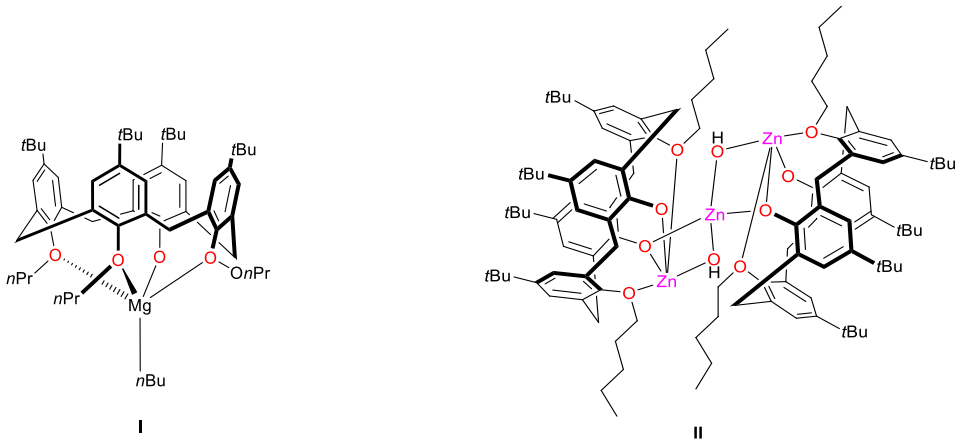


Figure S9. Known complexes **I** and **II.**

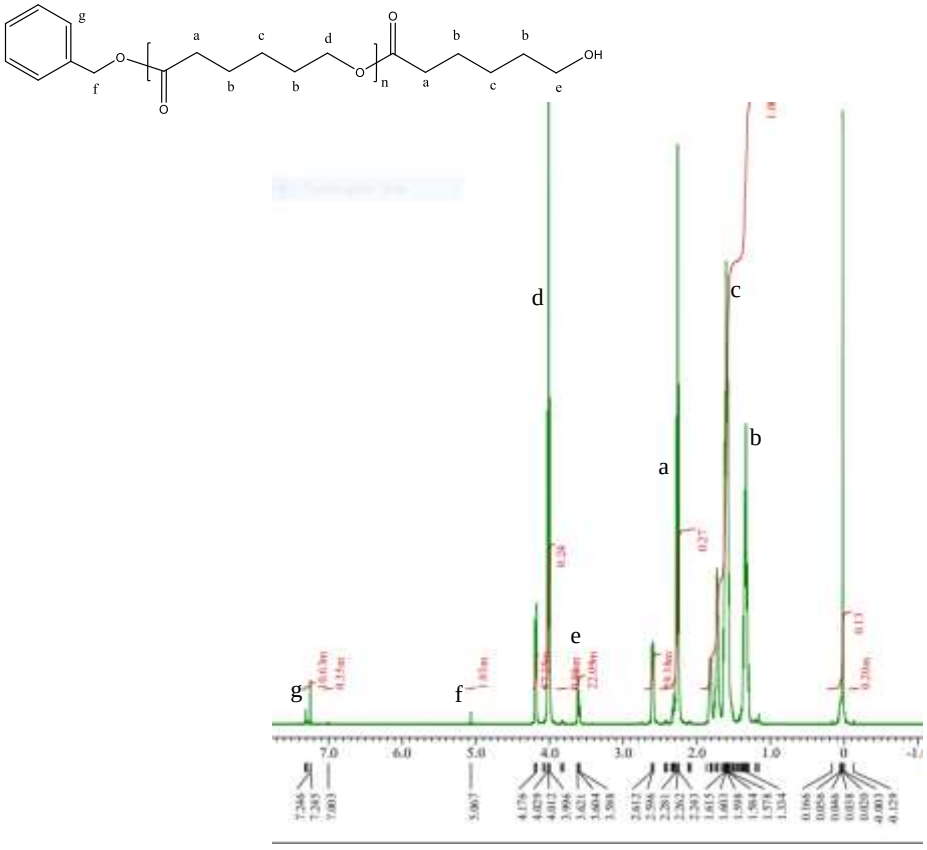
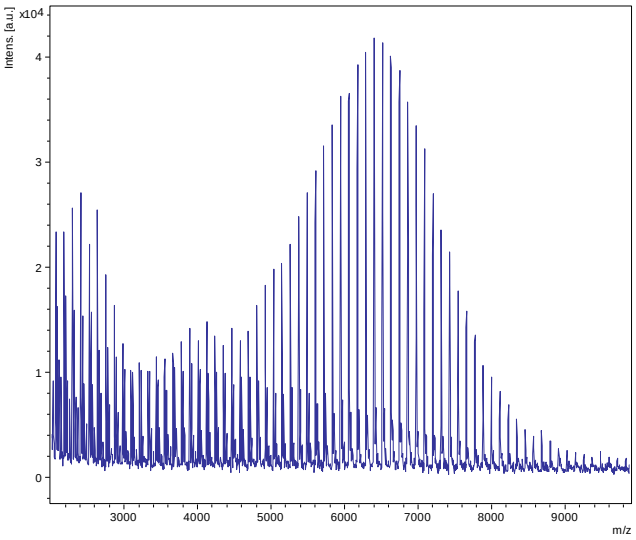
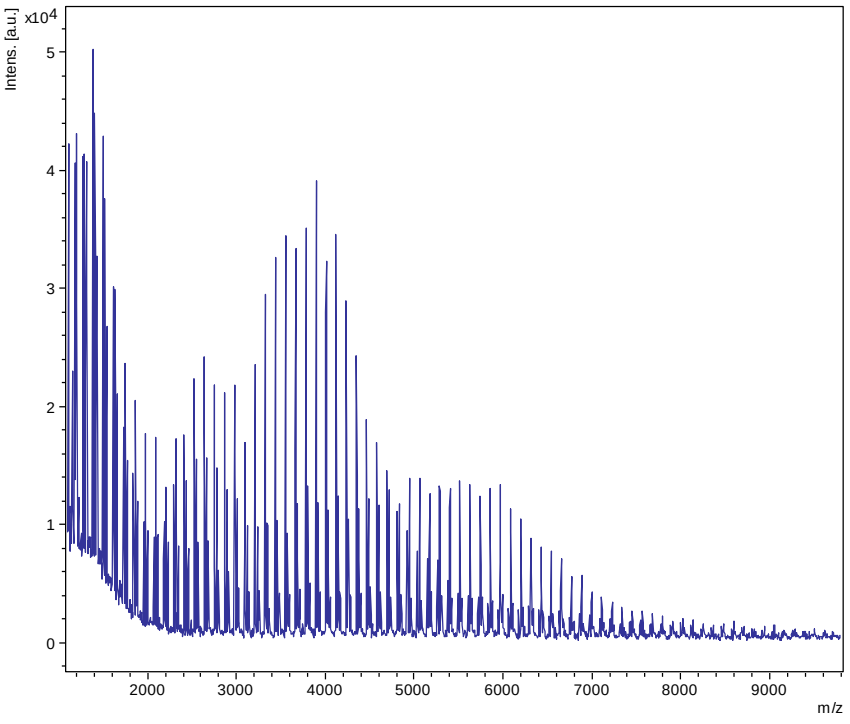


Figure S10. ^{1}H NMR spectrum of PCL synthesised with **4** (entry 23, Table S2).



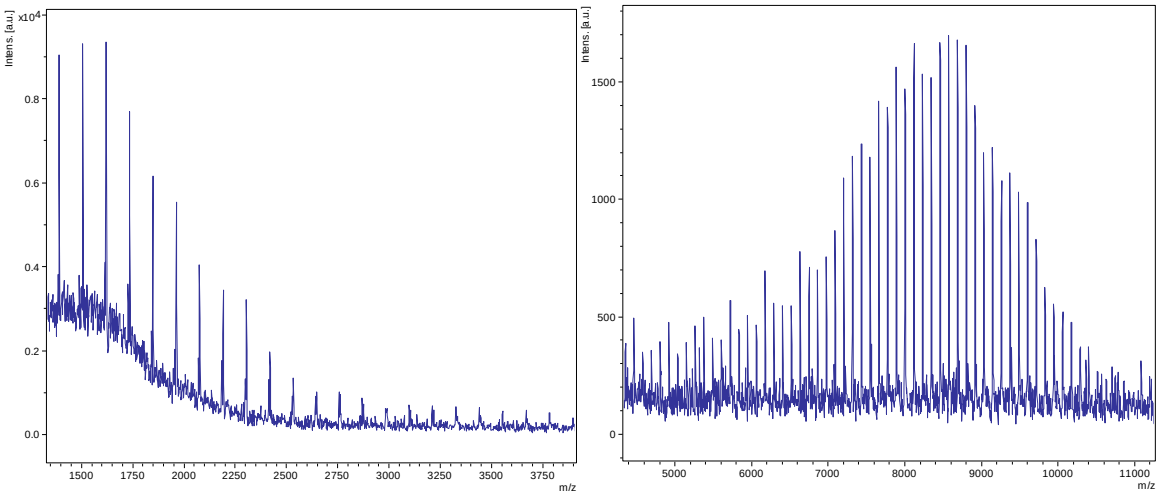
n	Calc	Obs
20	2323.8	2322.1
24	2780.4	2778.1
55	6402.8	6402.0
60	6973.4	6972.1

Figure S11. MALDI-ToF mass spectrum of PCL synthesised with **1** (entry 1, Table S2). The lower mass series are assigned as the sodium exchange artefact of HO-/-H polymers [M = 17 (OH)+1 (H) + n × 114.14 (CL) + 22.99 (Na^+)] (e.g., 2324 for n = 20, 2380 for n = 24). The higher mass family are assigned to BnO-/-OH terminated polymers (e.g., 6403 for n = 55, 6973 for n = 60).



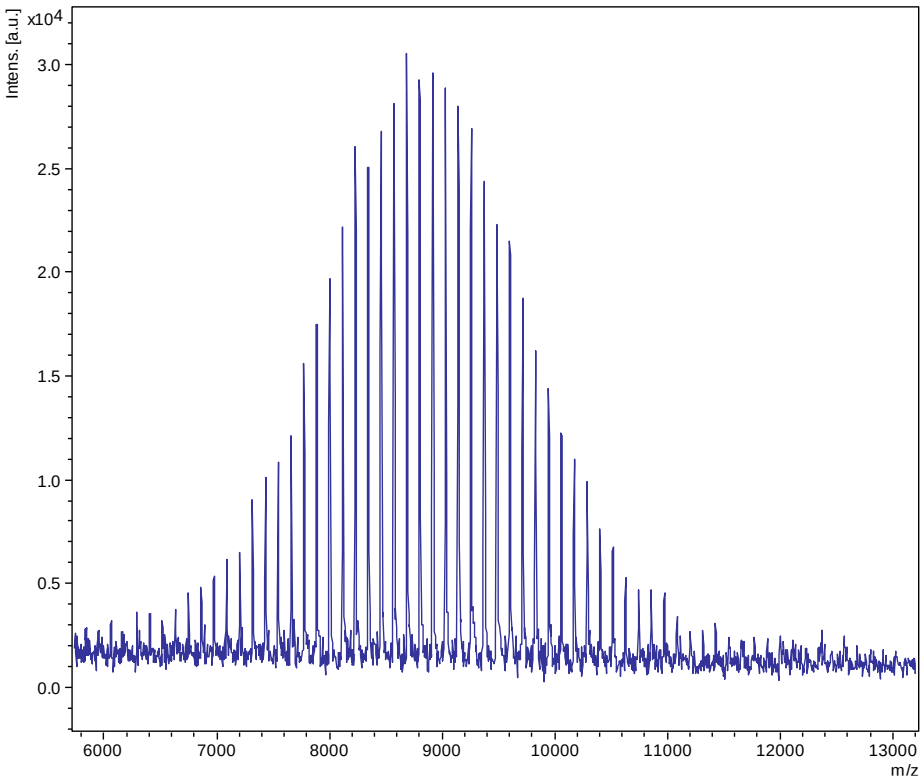
n	Calc	Obs
15	1753.1	1752.2
17	1981.4	1980.3
18	2095.5	2094.3
26	3098.7	3096.5
28	3327.0	3324.4
29	3441.1	3438.4
30	3555.2	3552.5

Figure S12. MALDI-ToF mass spectrum of PCL synthesised with **2** (entry 11, Table S2). Chain polymers (terminated by 2OH) [M = 17 (OH)+1 (H) + n × 114.14 (CL) + 22.99 (Na^+)] (e.g., peak 1753 for n = 15), plus a family of polymers with BnO end groups off-set by *ca*. 2.2 – 2.7Da [M = n × 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g., 3098 for n = 26).



n	Calc	Obs
12	1500.7	1501.2
60	6979.4	6978.2
80	9262.2	9261.1

Figure S13. MALDI-ToF spectrum using **3** in the presence of BnOH under N_2 (entry 18, table S2). For low molecular weight family, polymers present with BnO end groups [M = n × 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g., 1501 for n = 12); for higher molecular weight polymer, have BnO end groups [M = n × 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g., 5838 for n = 50, 6979 for n = 60).



n	Calc	Obs
60	6979.4	6979.5
70	8120.8	8119.6
80	9262.2	9262.6
90	10403.6	10405.1

Figure S14. MALDI-ToF mass spectrum of PCL synthesised with **4** (entry 23, Table S2). The main family are polymers with BnO end groups [M = n × 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g., peak 6979 for n = 60).

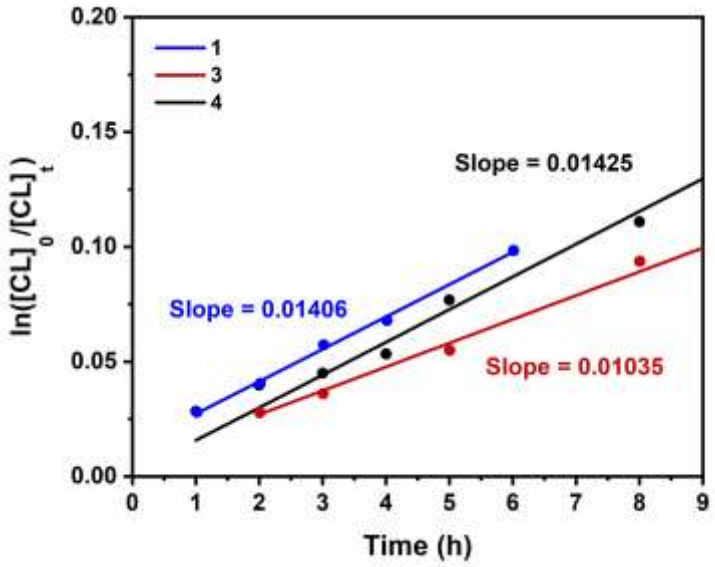
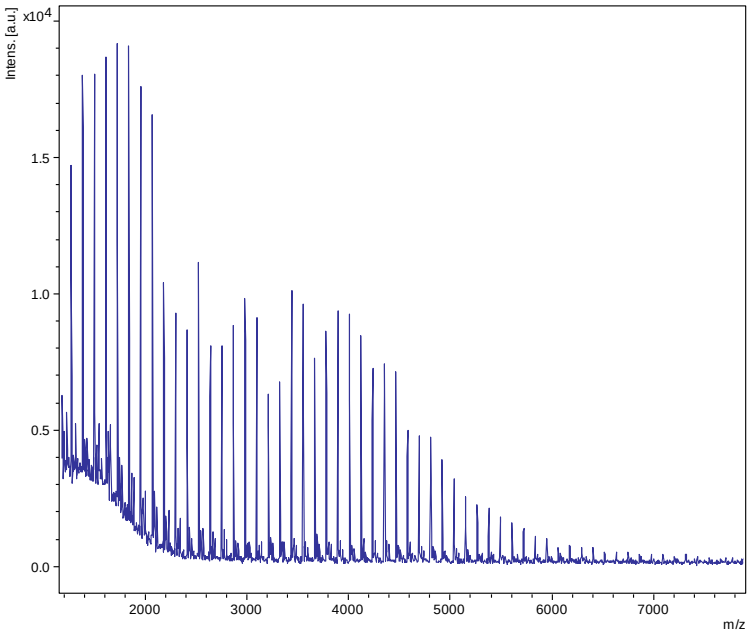


Figure S15. Plot of $\ln[CL]_0/[CL]_t$ *vs*. time for the polymerisation of ε-CL by using complexes **1**, **3**, and **4** in the presence of BnOH (conversions using **2** under the conditions employed for the kinetic study were too low to plot).

Table S3. ROP of ε-CL using **1** - **4** as melts

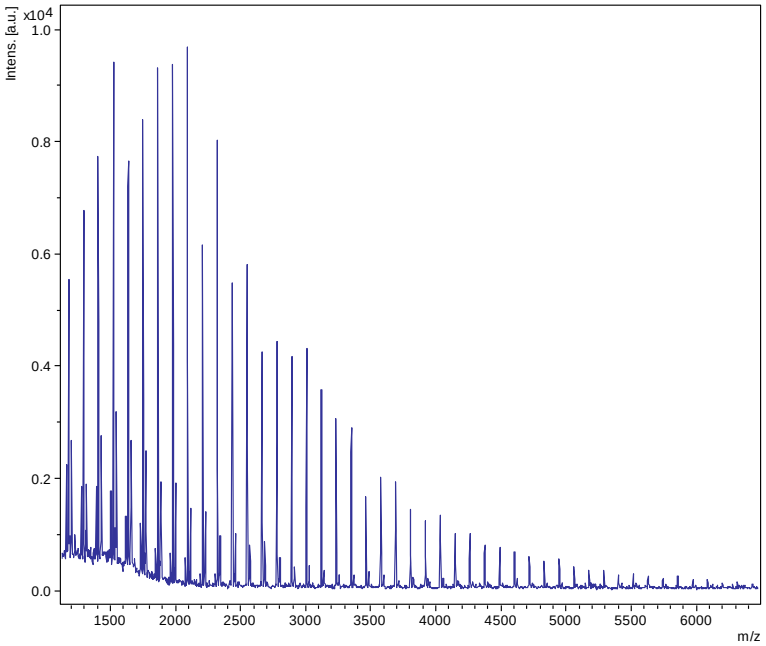
Entry	Catalyst	[CL]:[Cat]:BnOH	Conversion (%)[a]	M_n[b]	$M_n calc$[c]	Đ[d]
1	**1**	500:1:2	85	11030/1570	48620	1.84/1.15
2	**1**	500:1:0	77	17170/1280	43960	1.66/1.12
3*	**1**	500:1:2	36	35750	20650	1.61
4	**2**	500:1:2	42	23620/1410	24080	1.79/1.13
5	**2**	500:1:0	4	-	-	-
6*	**2**	500:1:2	7	-	-	-
7	**3**	500:1:2	11	-	-	-
8	**3**	500:1:0	7	-	-	-
9*	**3**	500:1:2	7	-	-	-
10	**4**	500:1:2	32	19140/1340	18370	1.34/1.10
11	**4**	500:1:0	12	-	-	-
12*	**4**	500:1:2	11	-	-	-

[a] Conducted over 24h at 130 °C. [b] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture. [b] Determined by GPC analysis calibrated with polystyrene standards and multiplied by correction factor of 0.56. [c] Calculated from ([CL]/Cat) × conv (%) × monomer molecular weight (M_{CL} = 114.14) + molecular weight of BnOH. [d] Polydispersity index (M_w/M_n) were determined by GPC. * Conducted in air.



n	Calc	Obs
12	1500.7	1500.2
18	2185.6	2184.6
24	2870.4	2868.8
26	3098.7	3096.9
30	3555.2	3553.0
50	5838.0	5837.5
55	6408.7	6407.7

Figure S17. MALDI-ToF mass spectrum of PCL synthesised with **1**/2BnOH as a melt (entry 1, Table S3). For low molecular weight family, polymers present with BnO end groups [M = n × 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g. 1501 for n = 12, 2870 for n = 24, 3096 for n = 26); for higher molecular weight polymer, have BnO end groups [M = n 114.14 (CL) + 108.05 (BnOH) + 22.99 (Na+)] (e.g. 5838 for n = 50, 6409 for n = 55).

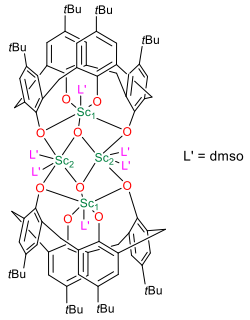
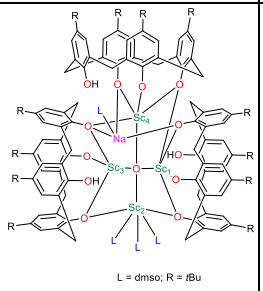
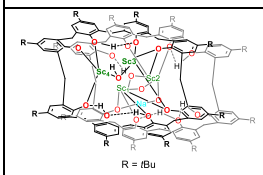
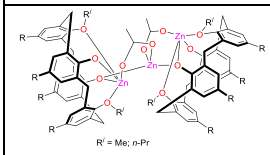
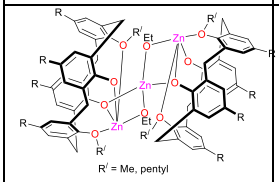
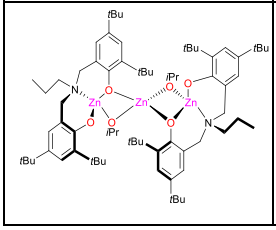


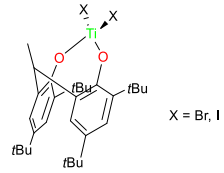
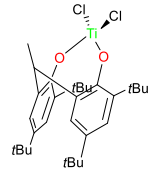
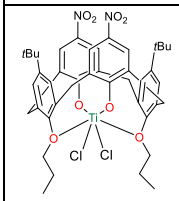
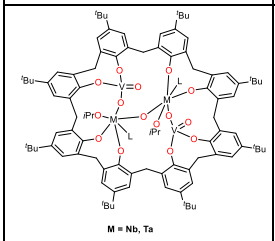
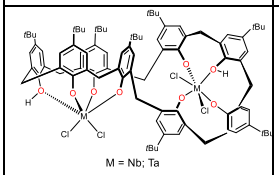
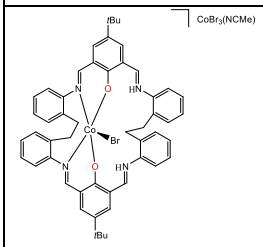
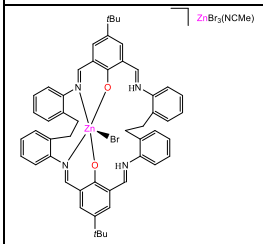
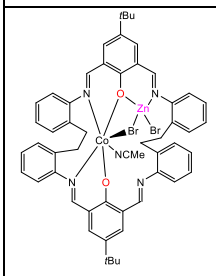
n	Calc	Obs
15	1753.1	1752.4
20	2323.8	2322.6
25	2894.5	2892.7

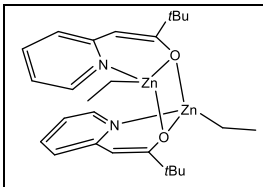
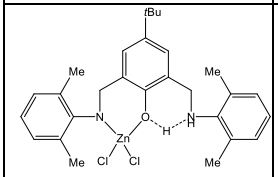
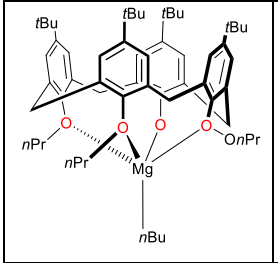
Figure S18. MALDI-ToF mass spectrum of PCL synthesised with **1** as a melt (entry 2, Table S3). Main peaks are chain polymer (terminated by 2 OH) as sodium adducts [M = 17 (OH) +

1(H) + n × 114.14 (CL) + 22.99 (Na+)] (e.g., peaks 1753 = 18 + (15 × 114.14+22.99) for n = 15, 2324 for n = 20).

Table S4. Comparison against catalysts screened using the same procedure/equipment.

Complex	ROP conditions	Conversion (%)	Polymer properties	Reference
 L' = dmso	200:1:1 130ºC 24h	11	-	*Dalton Trans*. 2021, **50**, 8302-8306.
 L = dmso; R = *t*Bu	200:1:0 130ºC 24h	77	Oligomeric	*Dalton Trans*. 2021, **50**, 8302-8306.
 R = *t*Bu	200:1:1 130ºC 24h	0	-	*Dalton Trans*. 2021, **50**, 8302-8306.
 R' = Me; *n*-Pr	500:1:2 90ºC 24h	R'=Me 79.7 R'= *n*-Pr 58.4	R'=Me M_n = 45590; Đ =1.18 R'= *n*-Pr M_n = 33430; Đ =1.16	*Dalton Trans*. 2022, **51**, 11776-11786.
 R' = Me, pentyl	500:1:0 90ºC 24h	R'=Me >99. R'= *n*-pentyl >99	R'=Me M_n = 2760; Đ =1.09 R'= *n*-pentyl M_n = 21275; Đ =2.59	*Dalton Trans*. 2022, **51**, 11776-11786.
	500:1:0 90ºC 24h	99.5	M_n = 17390; Đ =1.98	*Synthesis: Dalton Trans*, 2019, **48**, 13699-13710. *ROP of ε-CL: Dalton Trans*. 2022, **51**, 11776-11786.

 X = Br, I	250:1:2 130ºC 24h	R = Br >99 R = I >99	R=Br M_n = 5790; Đ =1.94 R= I M_n = 5640; Đ =1.30	*Dalton Trans*. 2020, **49**, 11978-11996.
	250:1:2 80ºC 24h	53	M_n = 6390; Đ =1.24	*Catal. Sci. Technol.* 2020, **10**, 1619-1639.
	250:1:2 80ºC 24h	24	M_n = 2540; Đ =1.13	*Catal. Sci. Technol.* 2020, **10**, 1619-1639.
 M = Nb, Ta	400:1:2 130ºC 24h	M = Nb 98 M = Ta 98.2	M=Nb M_n = 5150; Đ =1.18 M= Ta M_n = 2690; Đ =1.13	*Chem. Commun*. 2022, **58**, 7427-7430.
 M = Nb; Ta	800:1:2 130ºC 24h	M = Nb 72.3 M = Ta 96.7	M=Nb M_n = 3160; Đ =1.23 M= Ta M_n = 6150; Đ =1.59	*Chem. Commun*. 2022, **58**, 7427-7430.
	500:1:1 130ºC 24h	0	-	*Chem. Commun*. 2019, **55**, 11279-11282.
	500:1:1 130ºC 24h	0	-	*Chem. Commun*. 2019, **55**, 11279-11282.
	500:1:2 130ºC 24h	71.5	M_n = 3480; Đ =1.15	*Chem. Commun*. 2019, **55**, 11279-11282.

	400:1:1 35ºC 1h	89	M_n = 26600; Đ =1.17	Chen *et al*. *Dalton Trans.* 2017, **46**, 9846-9858.
	500:1:1 (+4MeLi)	99	M_n = 21700; Đ =1.27	Jie, Braunstein *et al*. *J. Organomet. Chem.* 2019, **882**, 1-9.
1	500:1:2 130ºC 24h	82	M_n = 16880; Đ =1.60	This work
2	500:1:2 130ºC 24h	66	M_n = 13460; Đ =1.57	This work
3	500:1:2 130ºC 24h	67	M_n = 39780; Đ =2.11	This work
4	500:1:2 130ºC 24h	81	M_n = 42080; Đ =1.53	This work
	500:1:1 130ºC 24h	6	-	This work

Supplementary references

[S1] (a) CrysAlysPRO software, Rigaku Oxford Diffraction 2019, 2020 & 2021. (b) SAINT (2008), and APEX 2 (2008) software for CCD diffractometers. Bruker AXS Inc., Madison, USA.

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