Electronic Supplementary Information

Mono-oxo molybdenum(VI) and tungsten(VI) complexes bearing chelating aryloxides: synthesis, structure and ring opening polymerization of cyclic esters.

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δ-Valerolactone

Table S2. ROP of δ-VL using complexes **1 – 9.**

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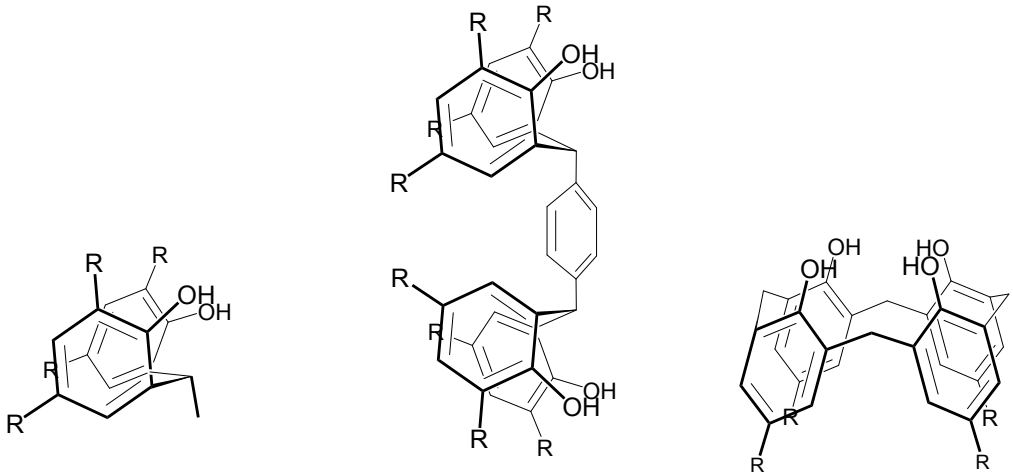


L^1H_2 L^2H_4 L^3H_4

Scheme 1. Phenols used in this study (R = *t*-Bu).

X-ray Crystallography

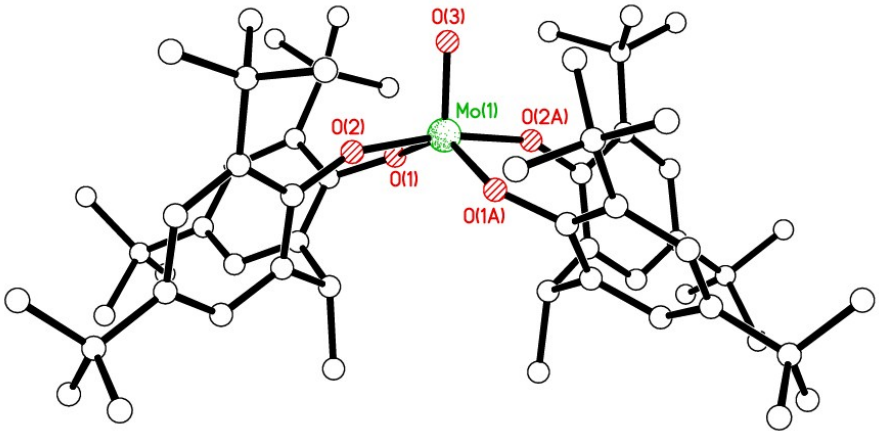


Figure S1. Alternative view of **1**.

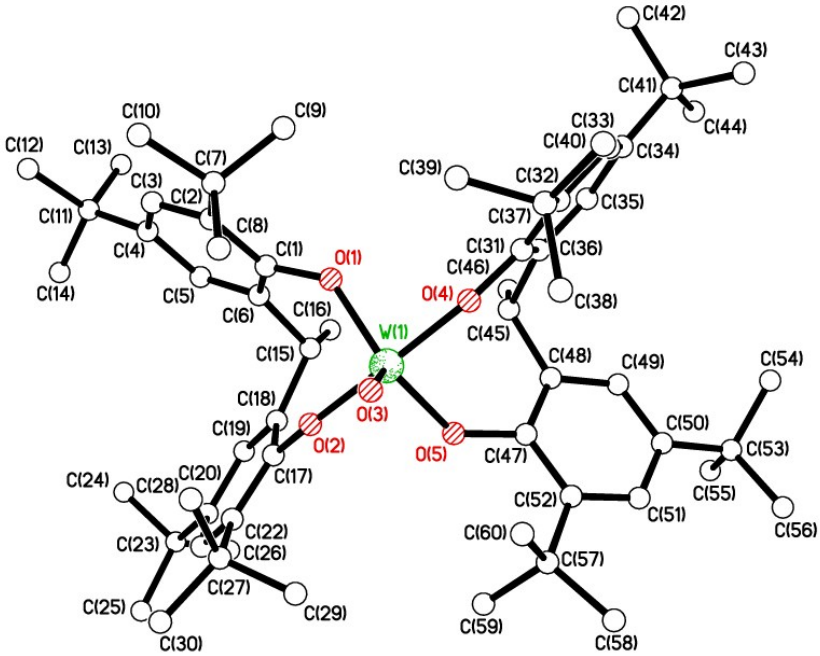


Figure S2. Alternative view of **2**.

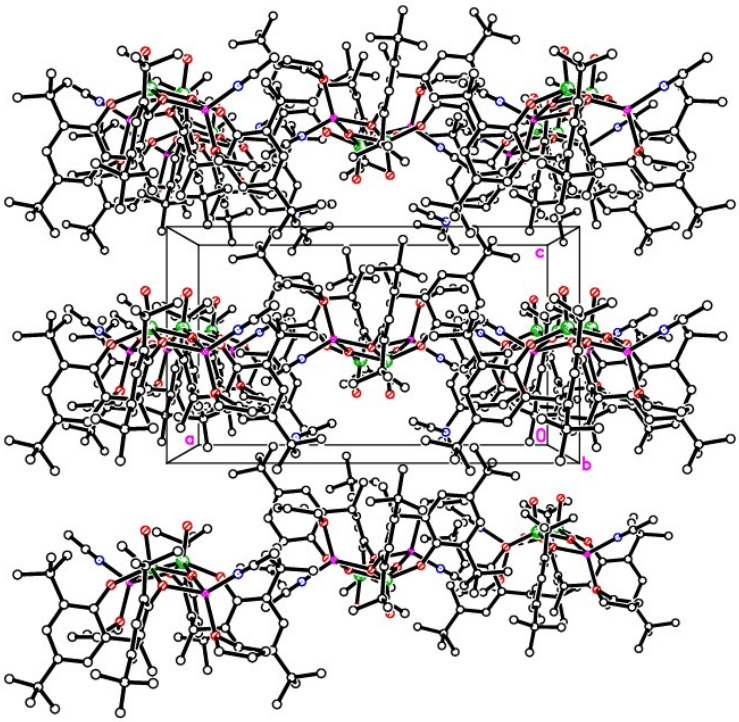


Figure S3. View of packing in **3**.

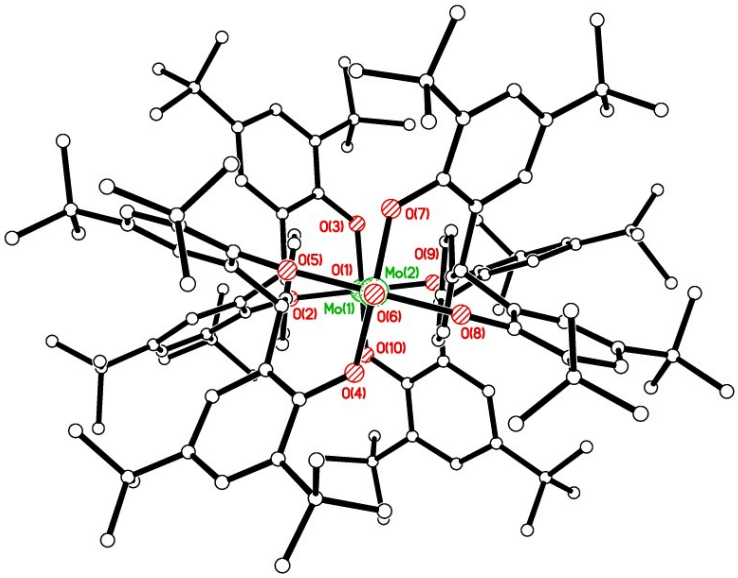


Figure S4. End-on view of **4** (that for **5** is very similar).

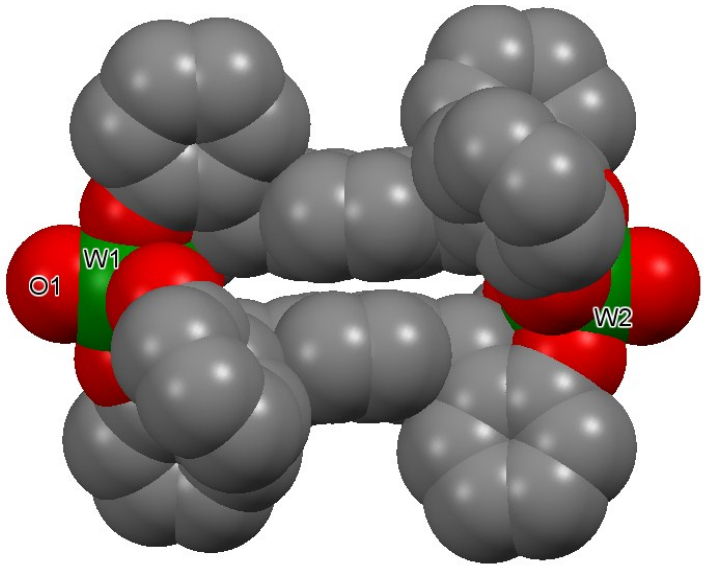


Figure S5. Space filling model of **5** (that for **4** is very similar).

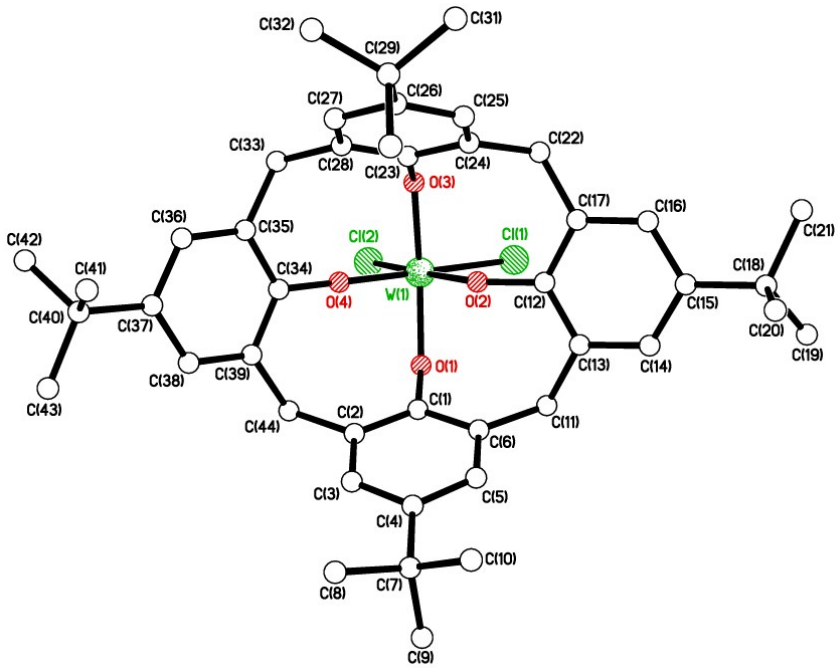


Figure S6. Alternative view of **7**.

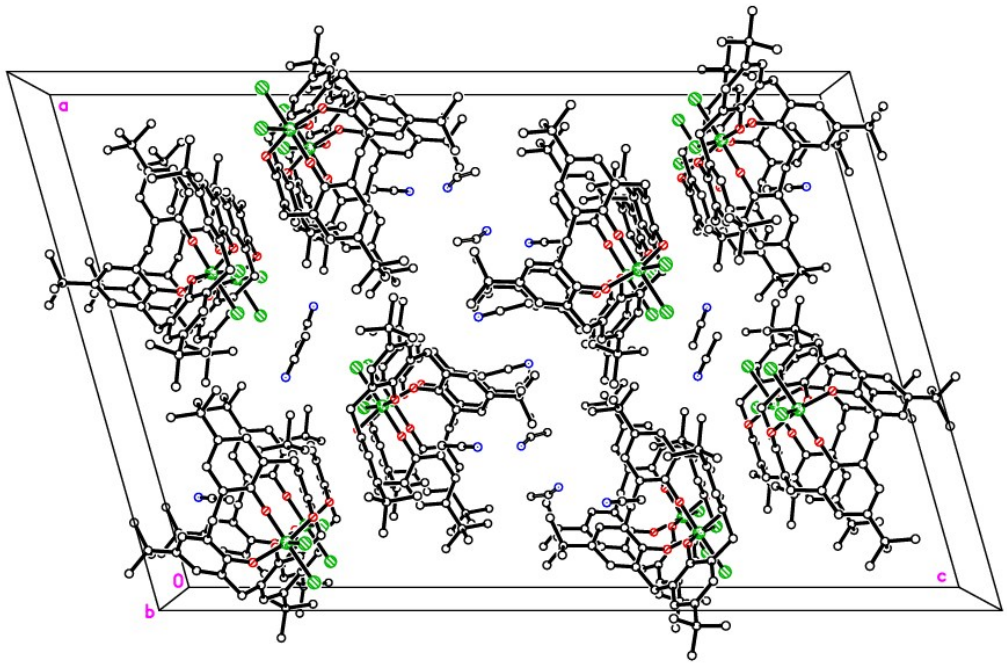


Figure S7. View of packing in **7**.

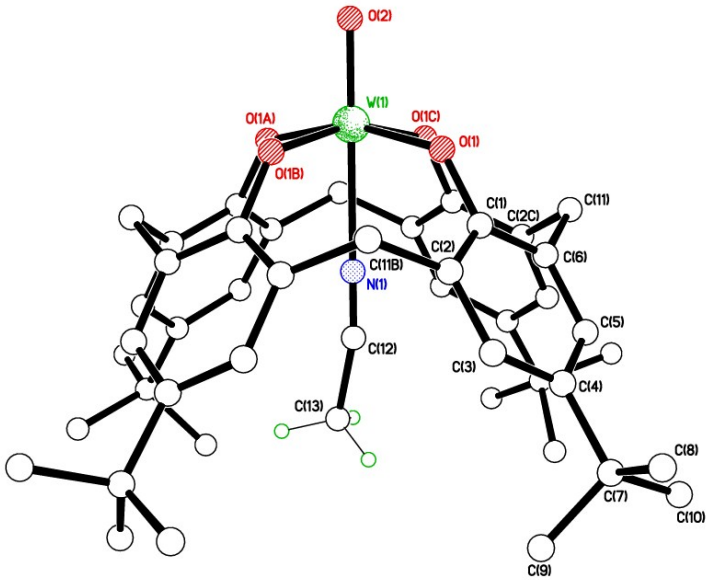


Figure S8. Alternative view of **8**.

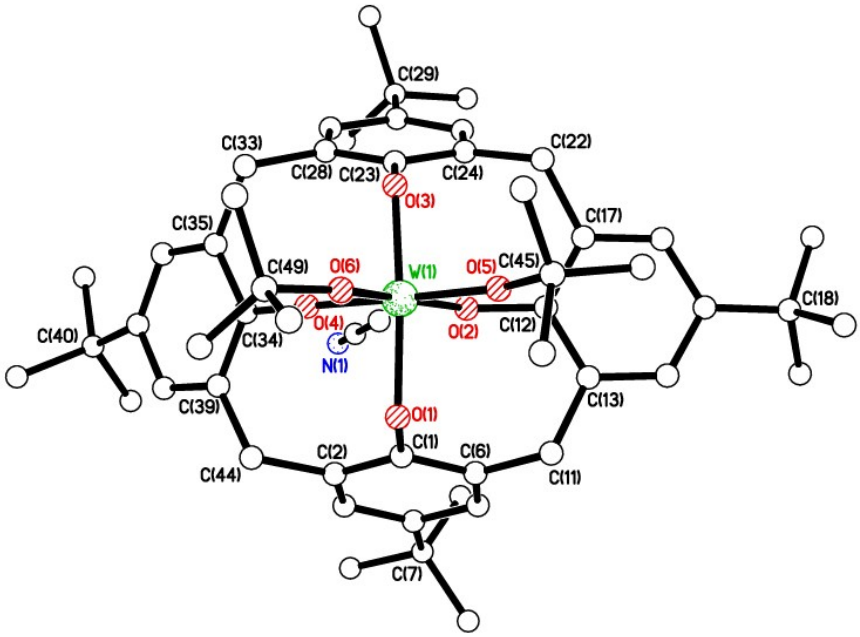


Figure S9. Alternative view of **9**.

ROP studies

ε-caprolactone

Table S1. ROP of ε-CL using complex **1 - 9**

Run	Cat.	ε-CL:M	T/℃	t/h	Conv.%[a]	*Mn*[b]	Mn_{Calcd}[c]	PDI[d]
1	**1**	250:1	130	24	99.1	24430	28190	2.26
2	**2**	250:1	130	24	98.6	5820	28140	1.32
3	**2**	500:1	100	24	98.9	20550	56440	1.76
4	**3**	250:1	130	48	97.5	38000	27820	1.85
5	**4**	250:1	130	24	99.6	29650	28420	1.60
6	**5**	250:1	130	24	94.6	21240	26990	1.76
7	**6**	250:1	130	24	99.1	5230	28280	1.12
8	**7**	250:1	130	48	99.3	3600	28340	1.61
9	**8**	250:1	130	48	94.5	4980	22970	1.10
10	**9**	250:1	130	24	39.0	5260	11130	1.10
11	**5**	500:1	130	48	99.5	11300	56780	1.67
12	**5**	1000:1	130	24	99.9	28990	114030	1.79
13	**5**	500:1	130	0.3	nothing	-	-	-
14	**5**	500:1	130	1	nothing	-	-	-

15	**5**	500:1	130	3	nothing	-	-	
16	**1**	500:1	15	48	trace	-	-	-
17	**1**	500:1	25	24	trace	-	-	-
18	**1**	500:1	50	48	96.9	16600	55300	3.29
19	**1**	500:1	60	24	93.1	24520	53130	1.29
20	**1**	500:1	80	24	97.7	38590	55760	1.98
21	**1**	500:1	100	24	98.9	22100	56440	2.04
22	**1**	500:1	110	24	99.3	37230	56670	2.26
23	**1**	500:1	130	1	98.1	37600	55990	2.02
24	**1**	500:1	130	5	99.4	37600	56730	1.97
25	**4**	500:1	14	48	-	-	-	-
26	**4**	500:1	25	24	67.0	-	-	-
27	**4**	500:1	50	48	99.3	11700	56670	1.43
28	**4**	500:1	60	24	90.5	6200	51650	1.33
29	**4**	500:1	80	24	99.5	8760	56780	1.30
30	**4**	500:1	100	24	99.8	12200	56960	2.09
31	**4**	500:1	130	1	99.4	9200	56730	1.59
32	**4**	500:1	130	3	99.1	9700	56560	1.79
33	**4**	500:1	130	5	98.7	12300	56330	2.92
34	**4**	250:1	130	12	99.6	11800	28420	2.37
35	**4**	500:1	130	24	99.4	13200	56730	2.12
36	**4**	100:1	130	24	97.2	8800	11090	2.14
37	**4**	1000:1	130	24	99.6	20100	113680	2.28
38	**4**	1500:1	130	24	99.5	28300	170350	1.47
39	**5**	500:1	15	48	-	-	-	-
40	**5**	100:1	100	24	2.1	-	-	-
41	**5**	500:1	100	24	5.3	-	-	-
42	**5**	1000:1	100	24	1.7	-	-	-

[a] Determined by ^{1}H NMR spectroscopy. [b] M_n from GPC in THF and were corrected with a Mark-Houwink factor of 0.56. [c] Calculated from ($[Monomer]_o/[M]_o$) x conv. (%) x Monomer molecular weight. [d] From GPC.

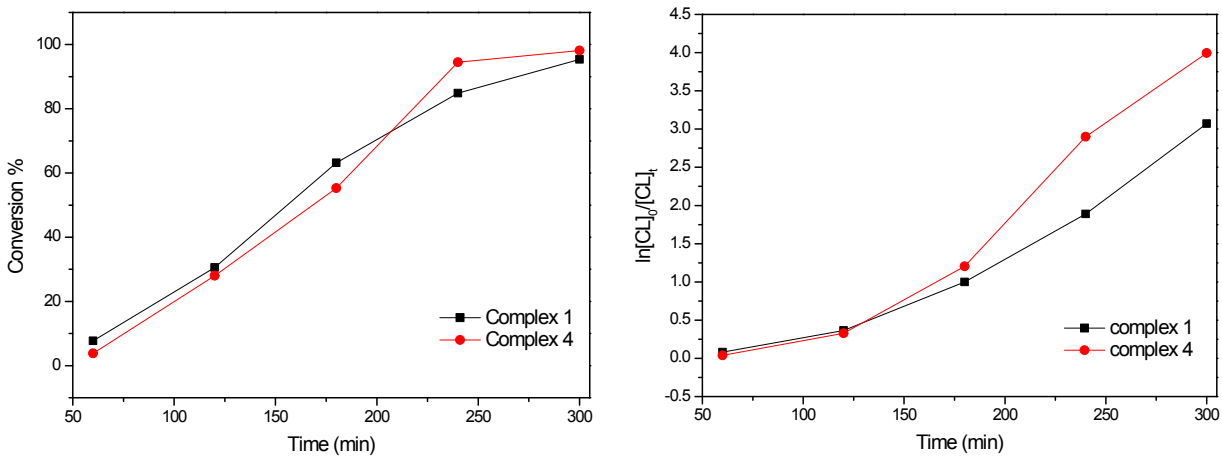


Figure S10. Left: Relationship between conversion and time for ROP of ε-CL at 130 °C using **1** and **4**; and Right: Plot of $\ln[CL]_0/[CL]_t$ *versus* time.

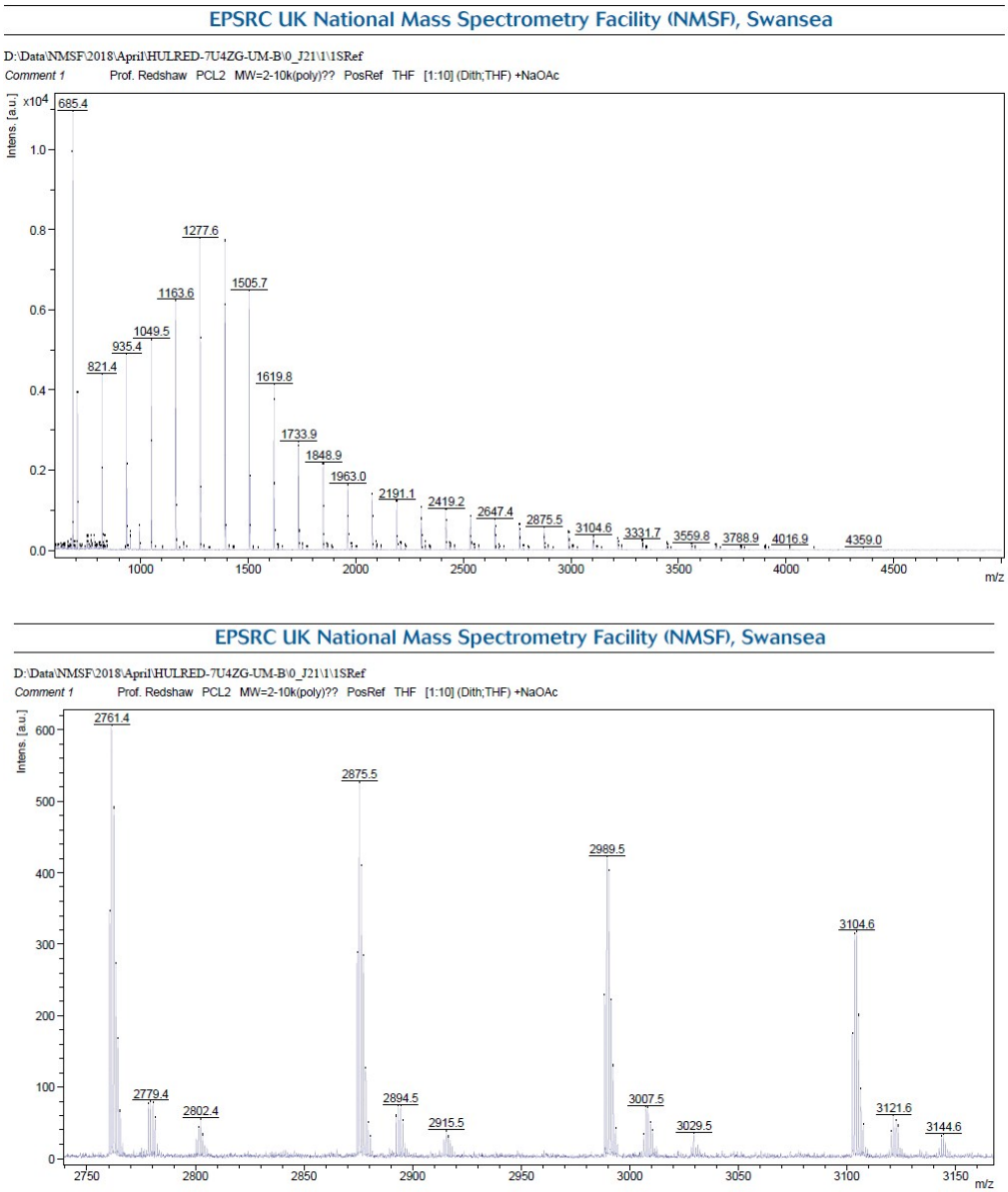


Figure S11. MALDI-ToF spectrum of PCL using **1** (run 21, Table S1). 100 °C, 24 h, 500:1

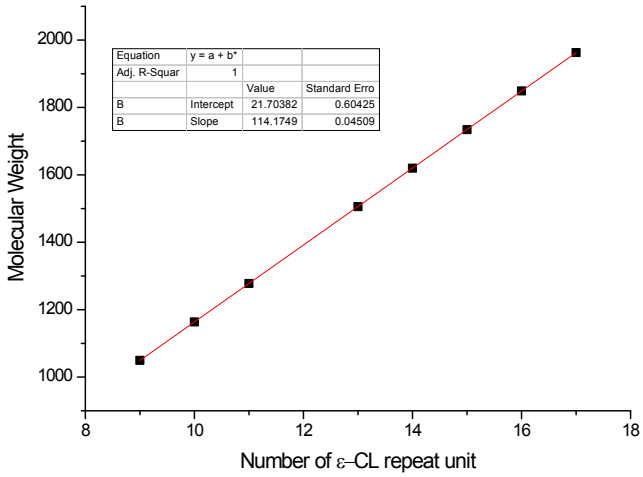


Figure S12. Plot of m/z values from MALDI-ToF spectrum *versus* the number of ε-CL repeat units for PCL using **1** (run 21, Table S1). 100 °C, 24 h, 500:1

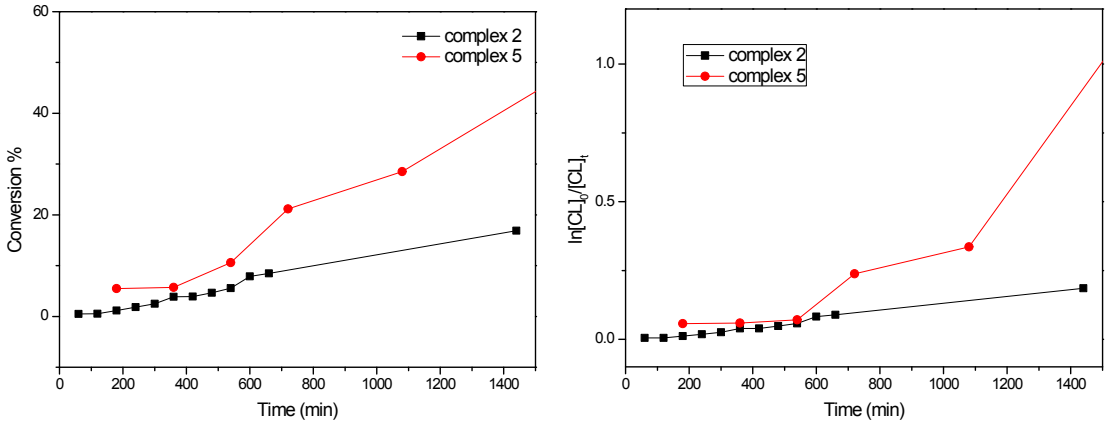
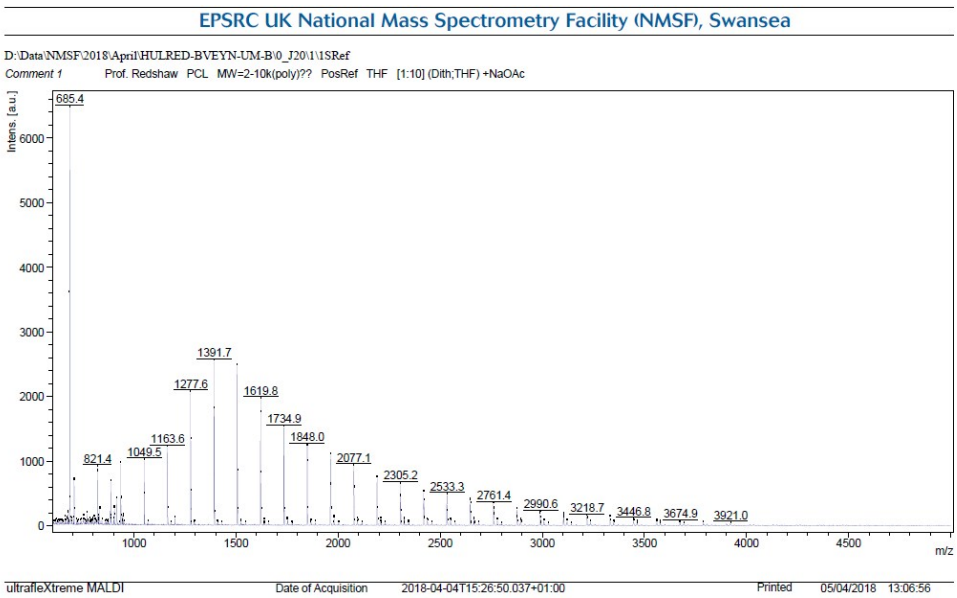


Figure S13. Relationship between conversion and time for ROP of ε-CL at 130 °C using **2** and **5**; and Plot of $\ln[CL]_0/[CL]_t$ *versus* time.



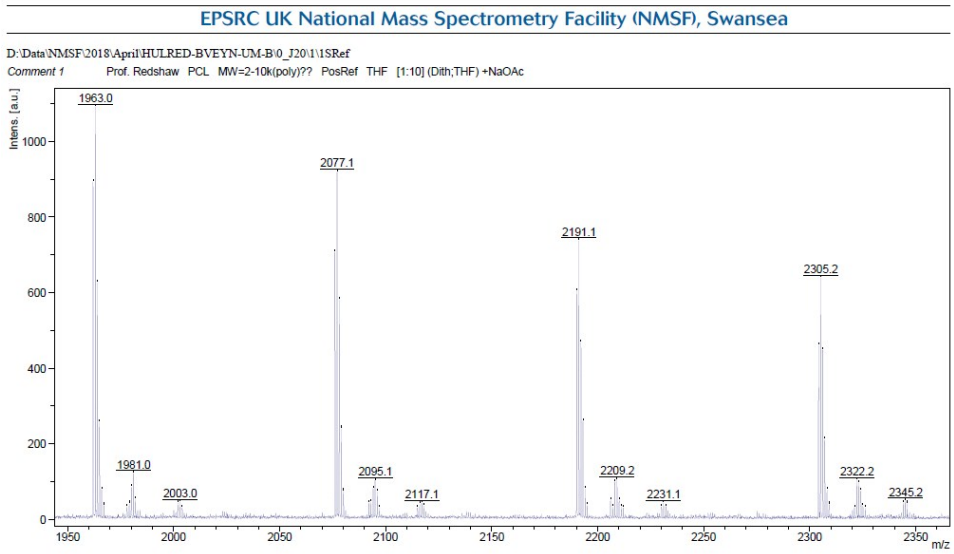


Figure S14. MALDI-ToF spectrum of PCL using **4** (run 32, Table S1).

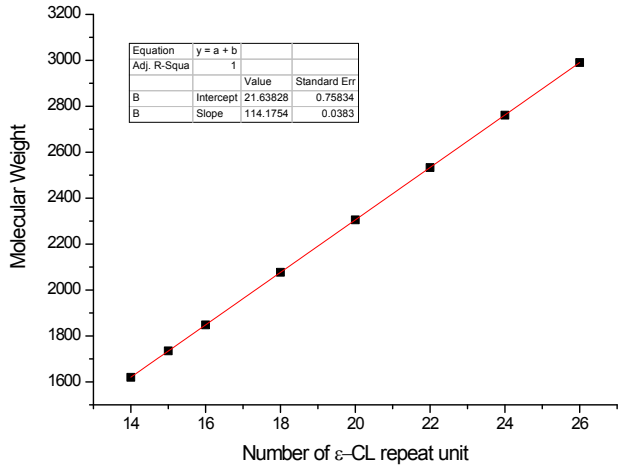


Figure S15. Plot of m/z values from MALDI-ToF spectrum *versus* the number of ε-CL repeat units for PCL using **4** (run 32, Table S1).

δ-Valerolactone

Table S2. ROP of δ-VL using complexes **1 - 9**

Run	Cat.	δ-VL:M	T/°C	t/h	Conv.%[a]	*Mn*[b]	Mn_{Calcd}[c]	PDI[d]
1	**1**	500:1	25	24	nothing	-	-	-
2	**1**	500:1	60	24	93.1	5700	46610	1.67
3	**1**	500:1	80	24	97.7	8640	48910	1.82
4	**1**	500:1	110	24	97.8	11100	48960	3.64
5	**1**	500:1	130	1	84.5	11470	42300	1.27
6	**1**	500:1	130	4	97.9	13100	49010	1.68
7	**1**	500:1	130	8	99.0	14800	49560	2.06
8	**1**	500:1	130	24	99.1	31000	49610	2.03

9	**1**	1000:1	130	24	97.4	12600	97520	2.41
10	**1**	2000:1	130	24	98.6	20900	197440	2.73
11	**1**	250:1	130	1	65.6	11470	16420	1.27
12	**1**	250:1	130	2	82.6	12050	20670	1.35
13	**1**	250:1	80	4	87.4	9600	21880	1.88
14	**1**	250:1	130	8	98.0	21340	24530	2.41
15	**1**	250:1	130	24	98.6	18900	24780	3.00
16	**2**	250:1	130	24	84.8	5290	21230	1.27
17	**2**	500:1	110	24	99.4	8410	49760	2.93
18	**2**	500:1	130	24	86.6	3500	43350	1.10
19	**3**	500:1	130	24	95.3	8020	47710	1.71
20	**4**	125:1	130	24	99.4	12880	12440	2.20
21	**4**	500:1	130	24	97.7	25400	48910	1.67
22	**4**	1000:1	130	24	99.6	11000	99720	3.17
23	**4**	2000:1	130	24	99.1	11100	198440	3.13
24	**5**	125:1	130	24	87.7	10380	10980	1.41
25	**5**	250:1	130	24	99.3	10510	24850	1.38
26	**6**	250:1	130	24	82.0	5240	20520	1.11
27	**7**	250:1	130	24	82.9	4870	20750	1.73
28	**8**	250:1	130	24	97.5	4630	24400	1.56
29	**9**	250:1	130	24	46.0	3210	11510	1.15

[a] Determined by ^{1}H NMR spectroscopy. [b] M_n from GPC in THF and were corrected with a Mark-Houwink factor of 0.57. [c] Calculated from ([Monomer]$_o$/[M]$_o$) x conv. (%) x Monomer molecular weight. [d] From GPC. [e] low yield.

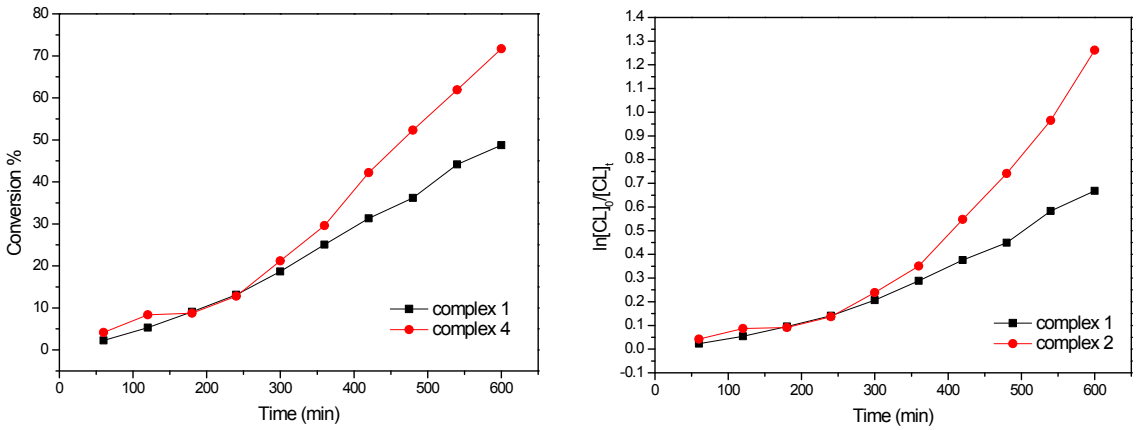


Figure S16. Left: Relationship between conversion and time for ROP of δ-VL at 130 °C using **1** and **4**; and Right: Plot of ln[CL]$_0$/[CL]$_t$ *versus* time.

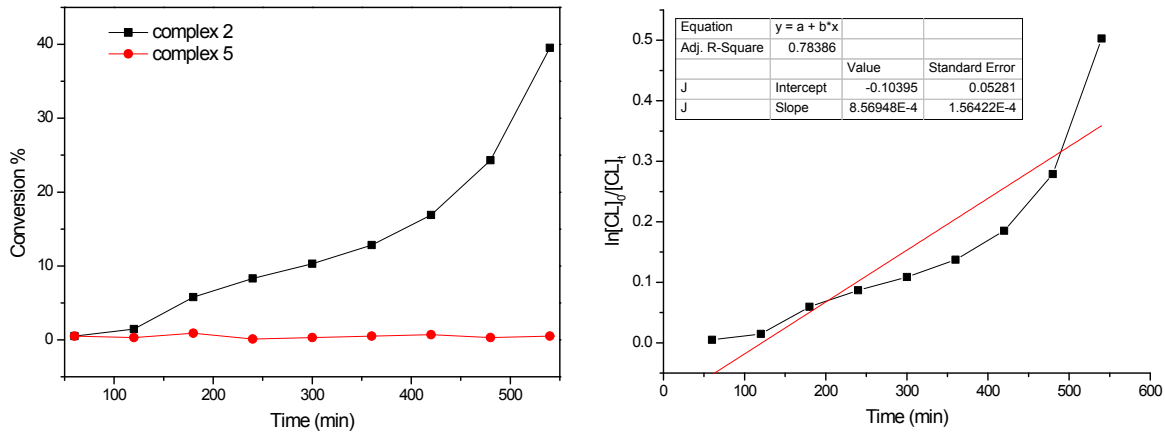


Figure S17. Left: Relationship between conversion and time for ROP of δ-VL at 130 °C using **2** and **5**; and Right: Plot of $\ln[CL]_0/[CL]_t$ *versus* time.

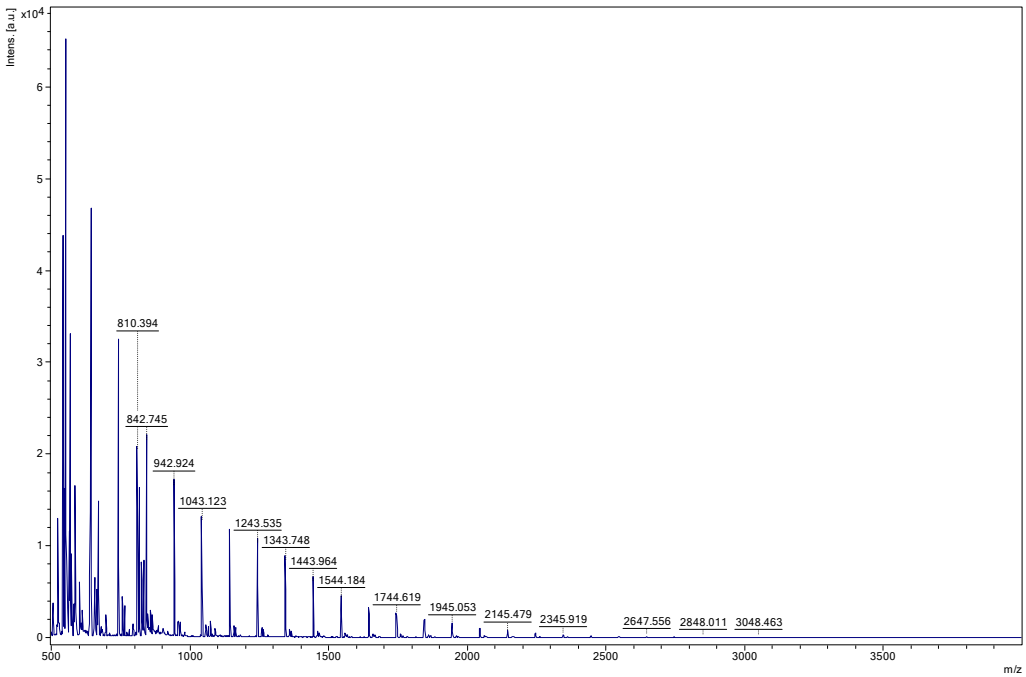


Figure S18. MALDI-ToF spectrum of PVL using **2** (run 17, Table S2), 110 °C, 24 h, 500:1 Peaks attributed to $H[O(CH_2)_4CO]_nOH$ in the presence of Na.