# Supporting Information

## Structural and Catalytic Studies of Grignard-Type Complexes with an Oxazoline-Amido-Phenolate Ligand: Influence of Halogen Ions

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# Crystal structure data

**Table S1.** Crystallographic data and refinement details for complexes **1-3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{76}H_{81}Cl_2Mg_4N_8O_{10}$ | $C_{42}H_{50}Br_2Mg_2N_4O_6$ | $C_{50}H_{68}I_2Mg_2N_4O_8$ |
| Fw | 1434.62 | 915.30 | 1155.50 |
| T, K | 150(2) | 150(2) | 150(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/_n$ | P-1 | P-1 |
| *a*, Å | 10.8220(19) | 9.9392(5) | 9.589(2) |
| *b*, Å | 18.680(3) | 13.5508(7) | 13.949(3) |
| *c*, Å | 18.011(3) | 17.0101(9) | 20.580(5) |
| α° | 90 | 102.2506(19) | 109.499(7) |
| *β* ° | 102.400(8) | 95.5112(19) | 98.510(7) |
| *γ* ° | 90 | 104.691(2) | 94.697(7) |
| *V*, Å$^3$ | 3556.1(10) | 2138.24(19) | 2540.7(10) |
| **Z** | 2 | 2 | 2 |
| $\rho_{calc}$, Mg/m$^3$ | 1.340 | 1.422 | 1.510 |
| μ(Mo Kα), mm$^{-1}$ | 0.192 | 1.975 | 1.318 |
| Reflections collected | 67660 | 43734 | 42609 |
| No. of parameters | 455 | 513 | 603 |
| Indep. reflns ($R_{int}$) | 8488 (0.0762) | 10134 (0.0371) | 10258 (0.0608) |
| Final R indices $R_1$[a], $wR_2$[a] | $R_1$= 0.0564, $wR_2$= 0.1475 | $R_1$= 0.0401, $wR_2$= 0.1052 | $R_1$= 0.0628, $wR_2$= 0.1502 |
| *R* indices(all data) | $R_1$= 0.0828, $wR_2$= 0.1681 | $R_1$= 0.0556, $wR_2$= 0.1173 | $R_1$= 0.0827, $wR_2$= 0.1681 |
| GoF [b] | 1.038 | 1.041 | 1.031 |

[a] $P1 = [\Sigma(|\Phi_0| - |\Phi_\chi|]/\Sigma|\Phi_0|]$; $\omega P2 = [\Sigma\omega(\Phi_0^2 - \Phi_\chi^2)^2/\Sigma\omega(\Phi_0^2)^2]^{1/2}$ , ω = 0.10.
[b] GoF = $[\Sigma w(F_0^2\text{-}F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

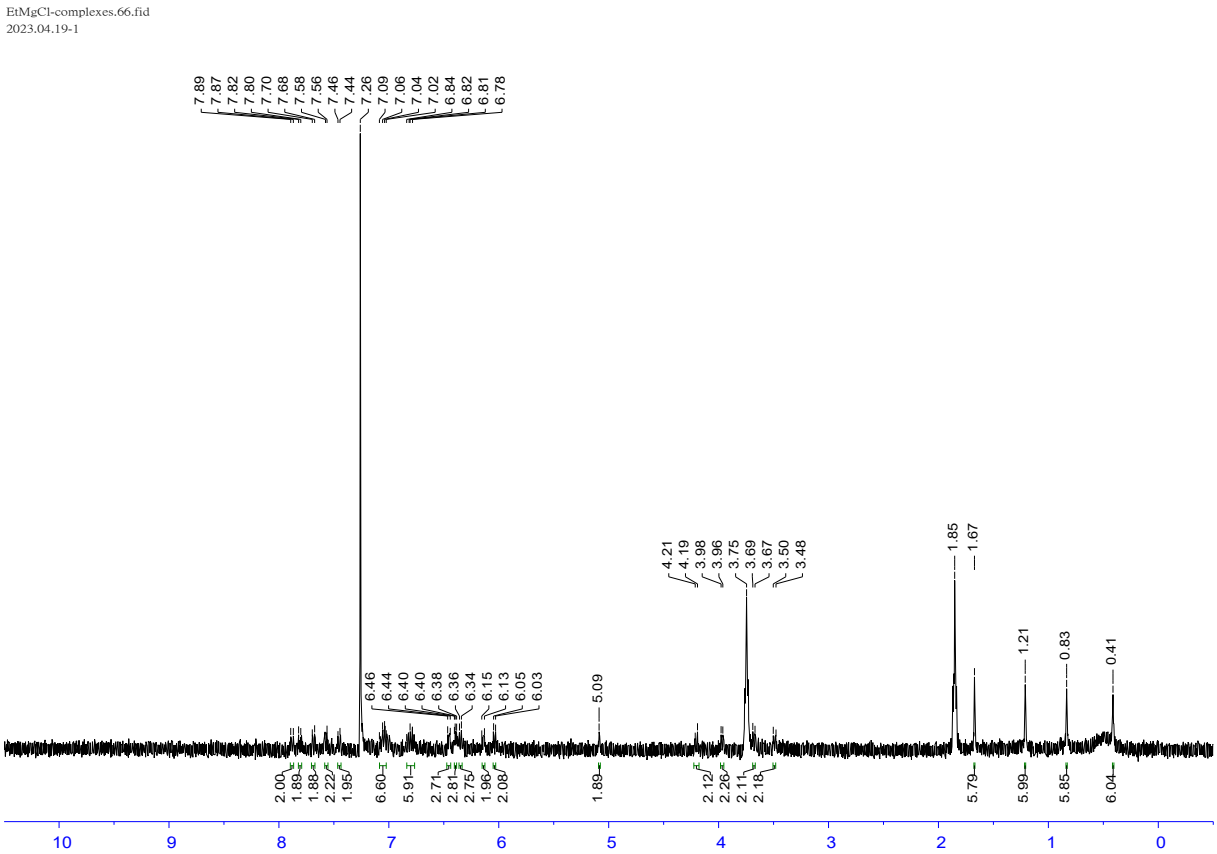



**Figure S1.** $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of complex **1**

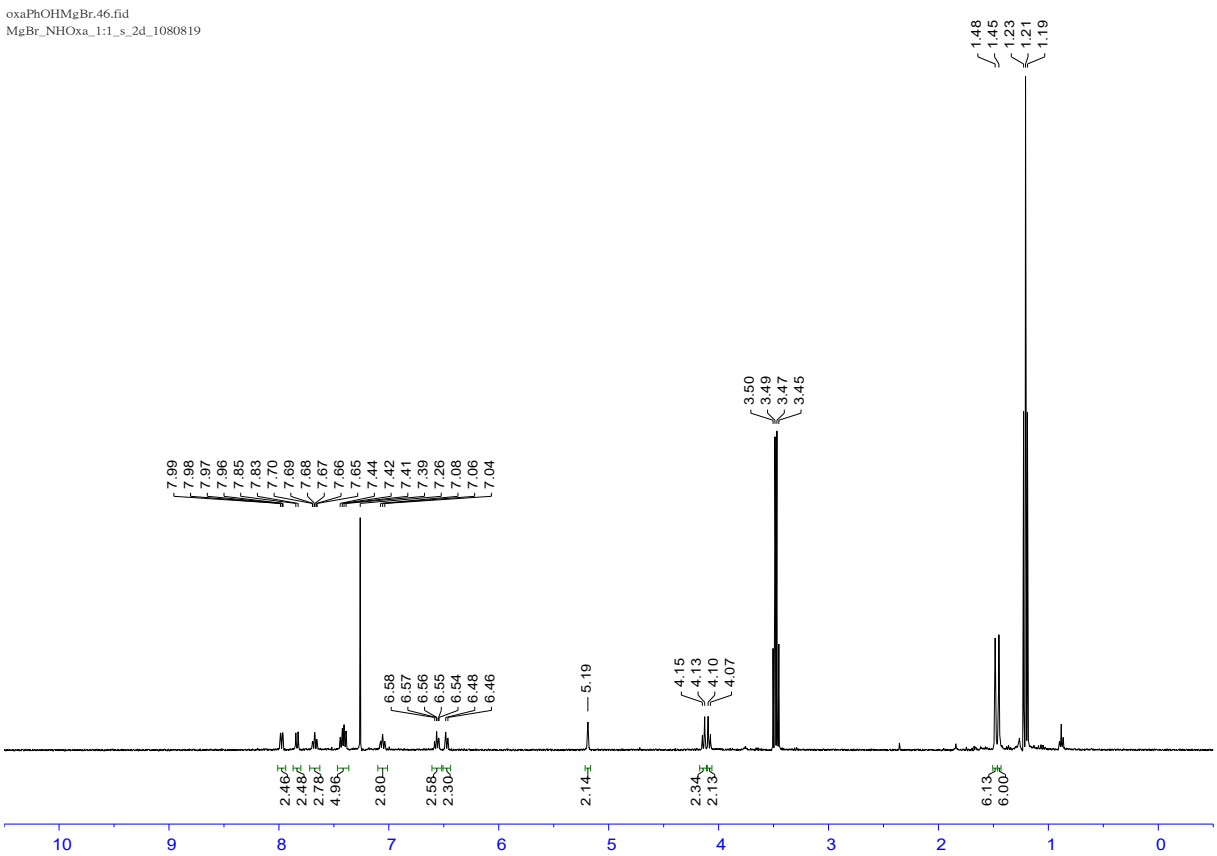



**Figure S2-1.** $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of complex **2**

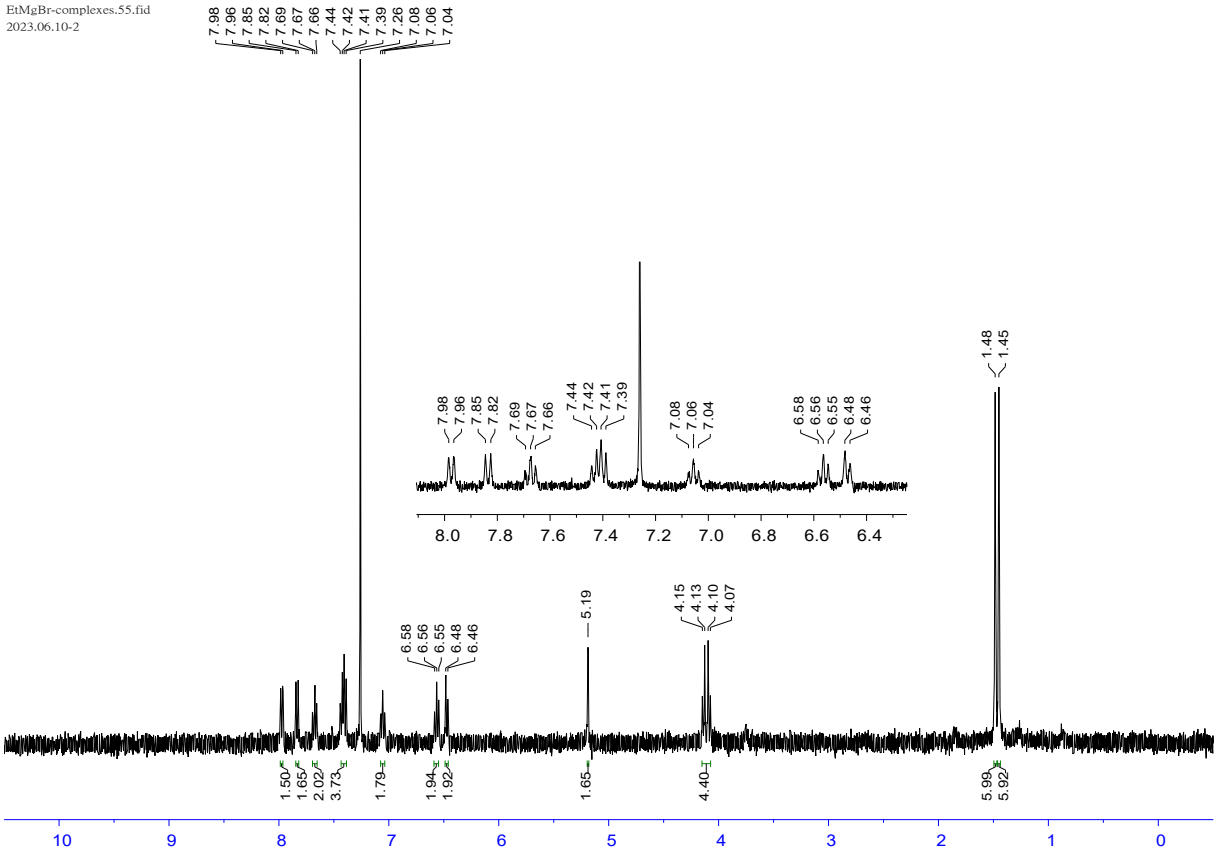



**Figure S2-2.** $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of complex **2**

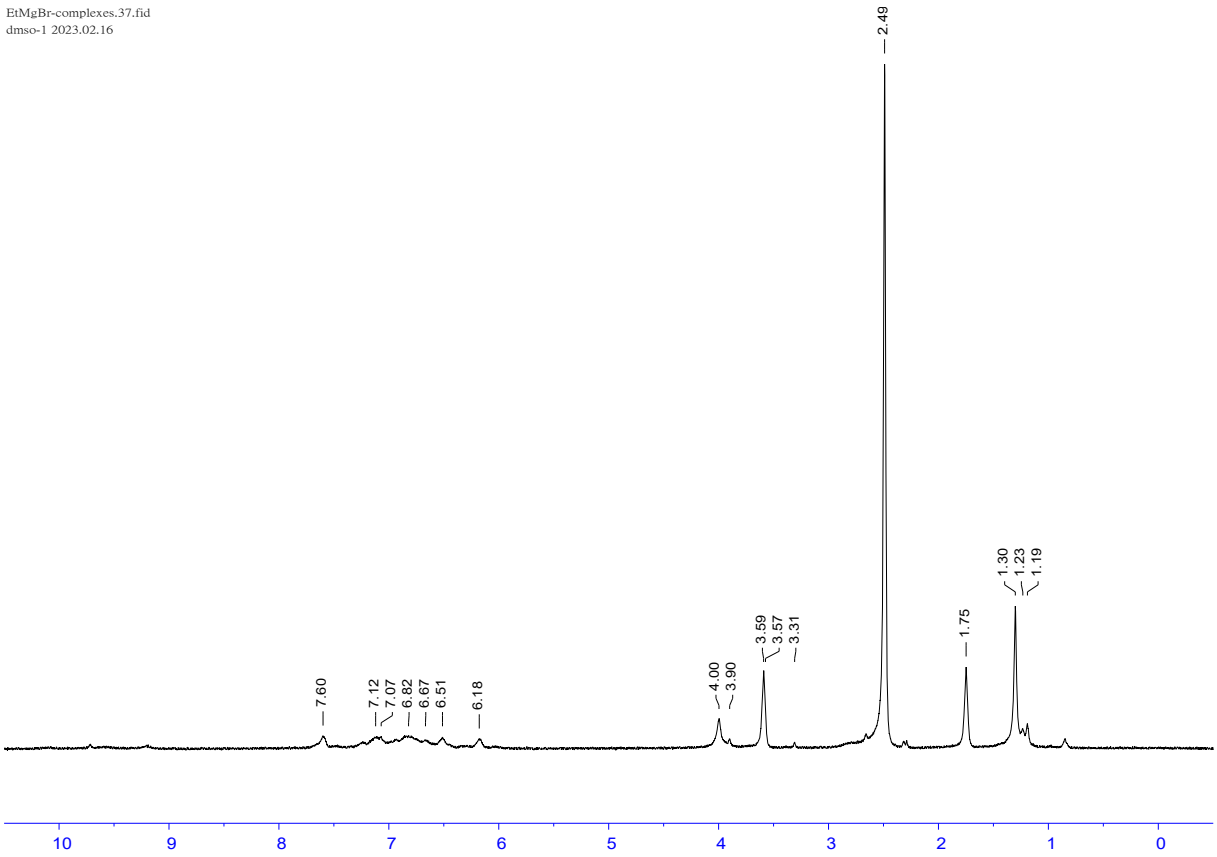



**Figure S2-3.** $^{1}$H NMR (400 MHz, DMSO-$d_6$, 298 K) of complex **2**

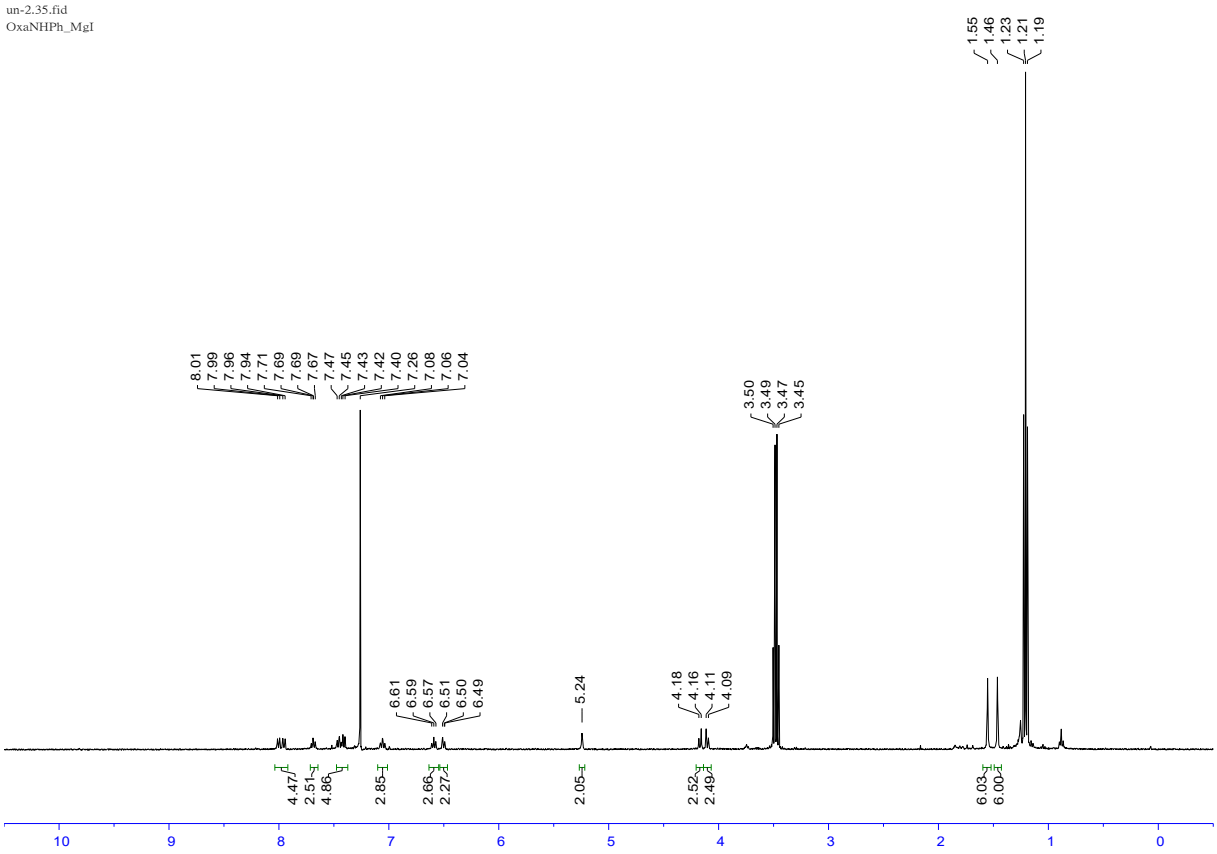



**Figure S3-1.** $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of complex **3**

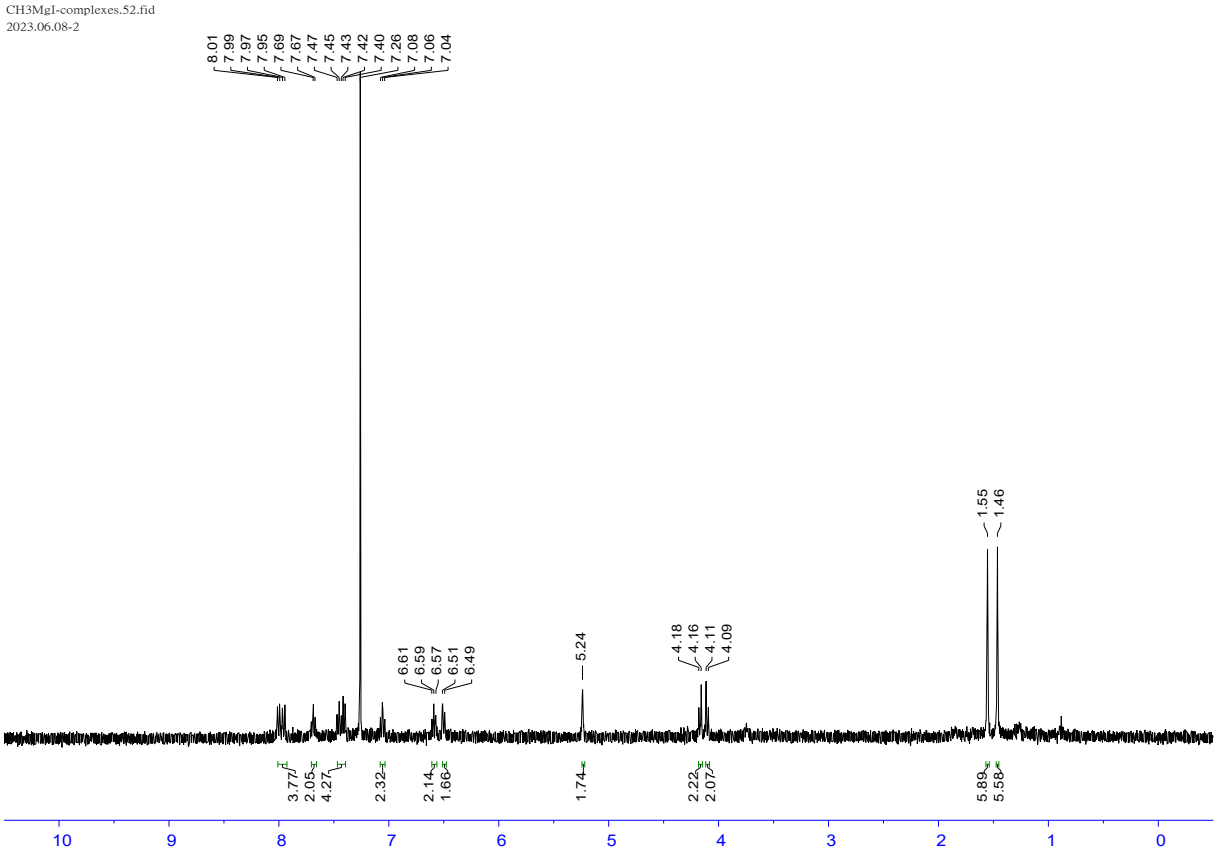



**Figure S3-2.** $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of complex **3**

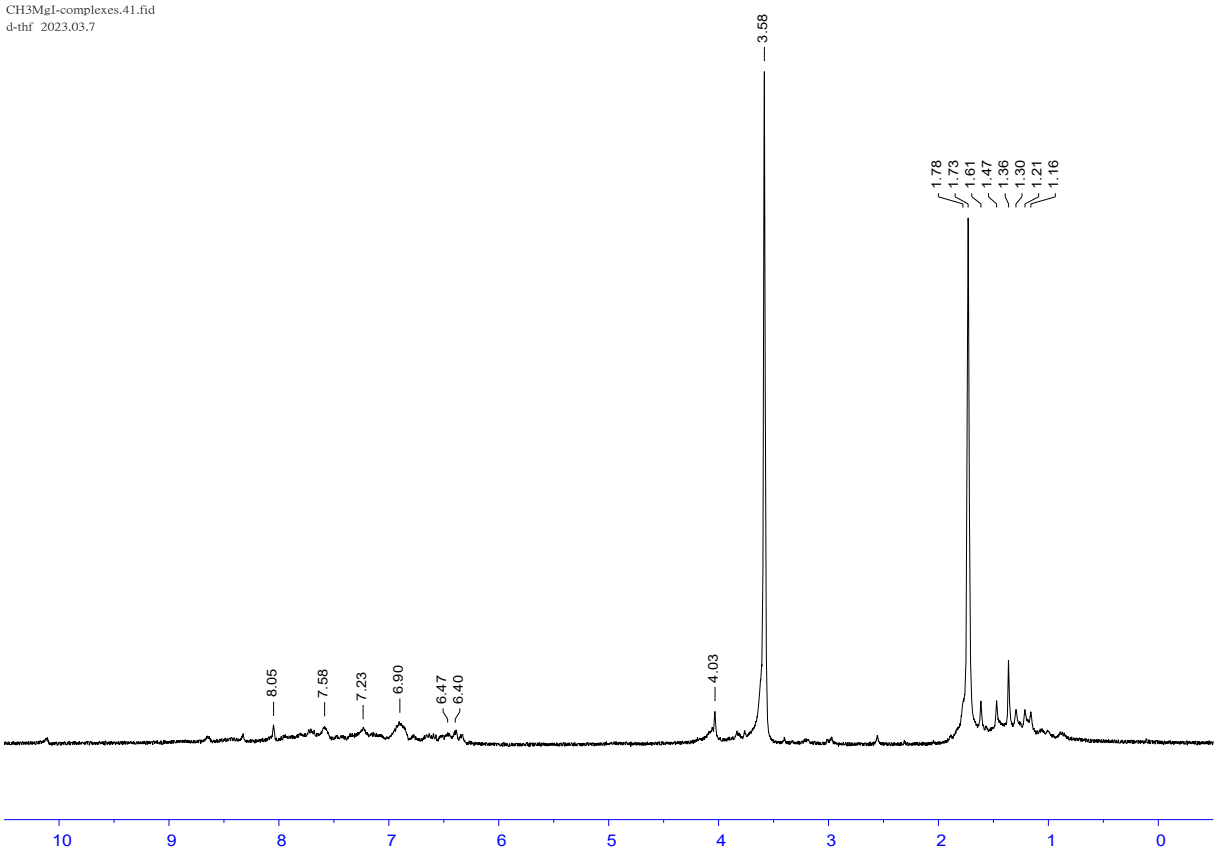
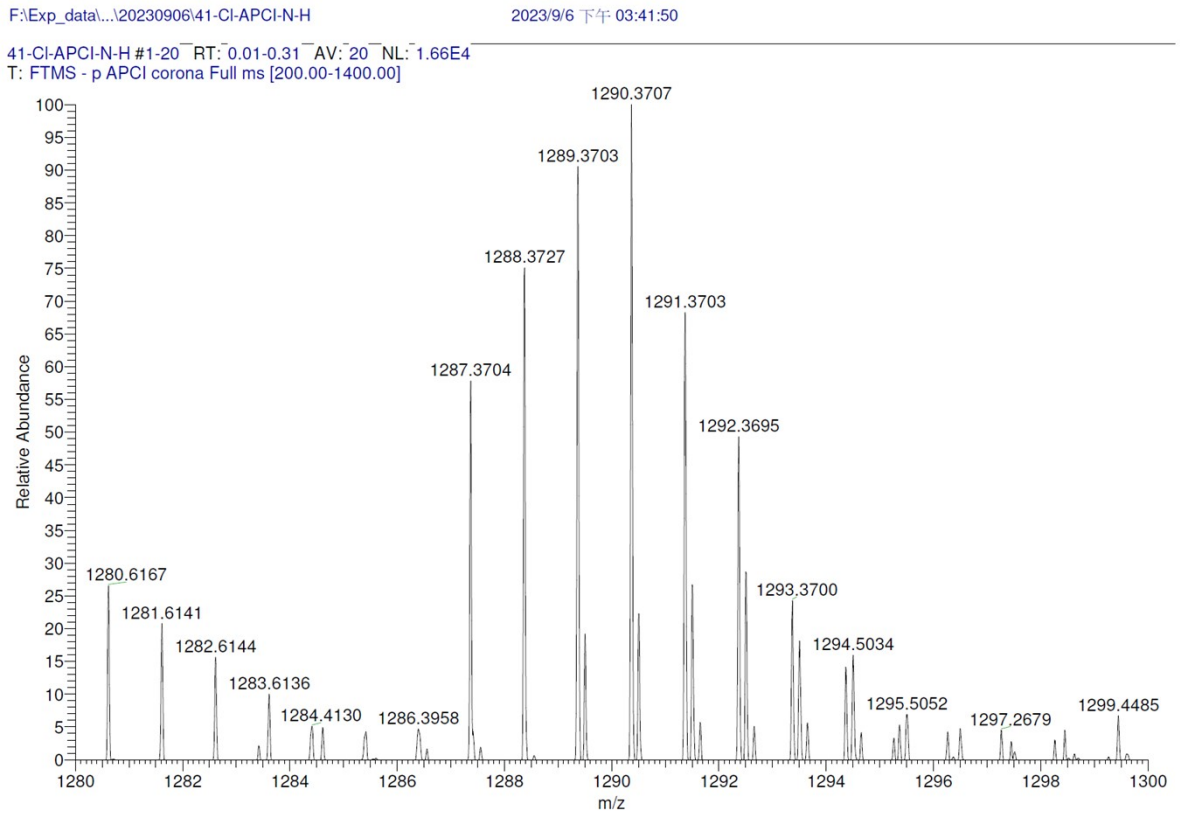



**Figure S3-3.** $^{1}$H NMR (400 MHz, THF-$d_8$, 298 K) of complex **3**




F:\Exp_data\...\20230906\41-Cl-APCI-N-H 2023/9/6 下午 03:41:50

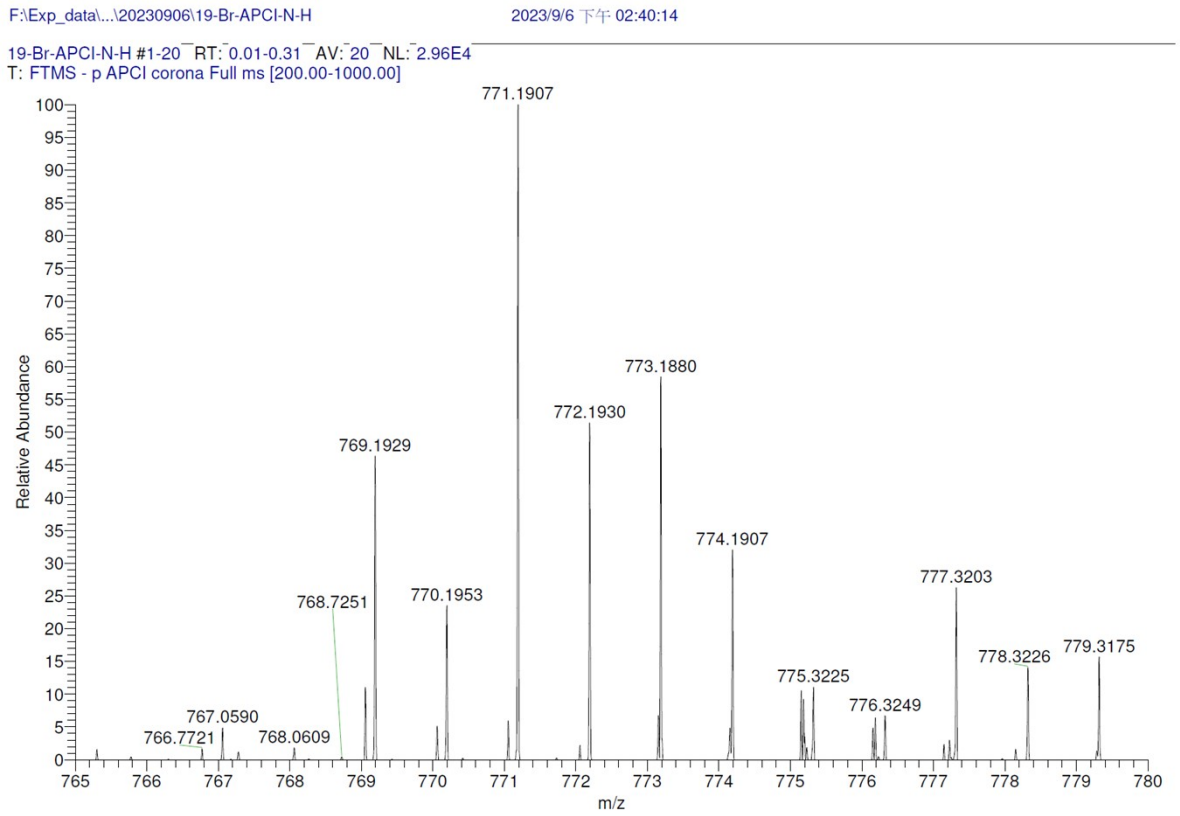
41-Cl-APCI-N-H#1-20 RT: 0.01-0.31 AV: 20
T: FTMS - p APCI corona Full ms [200.00-1400.00]
m/z= 1286.0902-1288.1203

| Isotope | Min | Max |
|---|---|---|
| N-14 | 8 | 8 |
| O-16 | 8 | 8 |
| C-12 | 68 | 68 |
| H-1 | 0 | 100 |
| Mg-24 | 4 | 4 |
| Cl-35 | 2 | 2 |

Charge 1
Mass tolerance 140.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1

| m/z | Intensity | Relative | Theo. Mass | Delta (ppm) | Composition |
|---|---|---|---|---|---|
| 1287.3704 | 9649.9 | 100.00 | 1287.3699 | 0.40 | $C_{68}H_{65}O_8N_8Cl_2Mg_4$ |

**Figure S4.** Atmospheric pressure chemical ionization (APCI) mass spectrum for complex **1**

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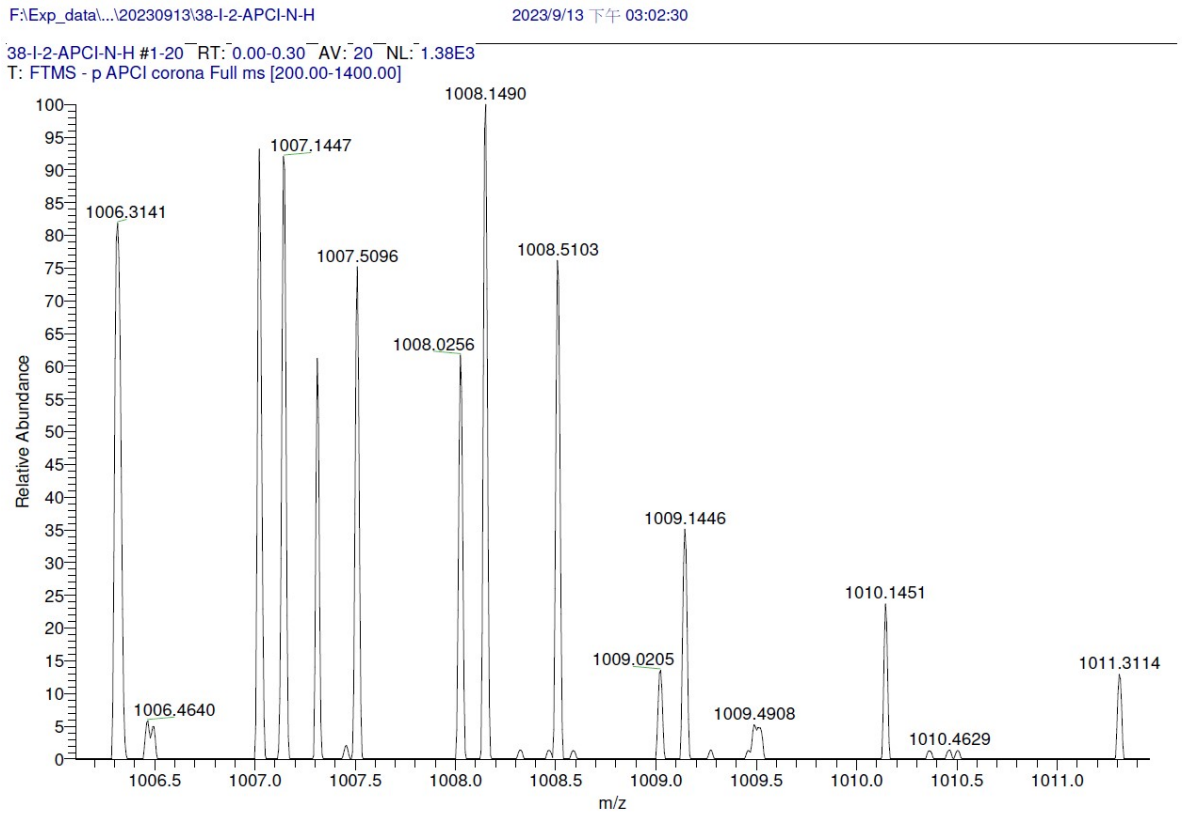
19-Br-APCI-N-H#1-20 RT: 0.01-0.31 AV: 20
T: FTMS - p APCI corona Full ms [200.00-1000.00]
m/z= 766.3583-767.7004

| Isotope | Min | Max |
|---|---|---|
| N-14 | 4 | 4 |
| O-16 | 4 | 4 |
| C-12 | 34 | 34 |
| H-1 | 0 | 100 |
| Mg-24 | 2 | 2 |
| Br-79 | 2 | 2 |

Charge 1
Mass tolerance 200.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1

| m/z | Intensity | Relative | Theo. Mass | Delta (ppm) | Composition |
|---|---|---|---|---|---|
| 767.0590 | 1469.2 | 100.00 | 767.0564 | 3.42 | $C_{34}H_{33}O_4N_4Br_2Mg_2$ |

**Figure S5.** Atmospheric pressure chemical ionization (APCI) mass spectrum for complex **2**




F:\Exp_data\...\20230913\38-I-2-APCI-N-H 2023/9/13 下午 03:02:30

38-I-2-APCI-N-H#1-20 RT: 0.00-0.30 AV: 20
T: FTMS - p APCI corona Full ms [200.00-1400.00]
m/z= 1006.1053-1011.4605

| Isotope | Min | Max |
|---|---|---|
| N-14 | 4 | 4 |
| O-16 | 6 | 6 |
| C-12 | 42 | 42 |
| H-1 | 0 | 110 |
| I-127 | 0 | 2 |
| Mg-24 | 0 | 2 |

Charge 1
Mass tolerance 200.00 ppm
Nitrogen rule not used
RDB equiv -1.00-100.00
max results 1

| m/z | Intensity | Relative | Theo. Mass | Delta (ppm) | Composition |
|---|---|---|---|---|---|
| 1008.1490 | 1414.6 | 100.00 | 1008.1515 | -2.46 | $C_{42}H_{50}O_6N_4I_2Mg_2$ |

**Figure S6.** Atmospheric pressure chemical ionization (APCI) mass spectrum for complex **3**


**Figure S7.** $^{1}$H NMR spectrum of PCL initiated by ε-CL/complex **1**/BnOH (150/1/1, Table 2, entry 1, $Mn_{(GPC)}$= 23.2 Kg/mol, $Đ$= 1.12)

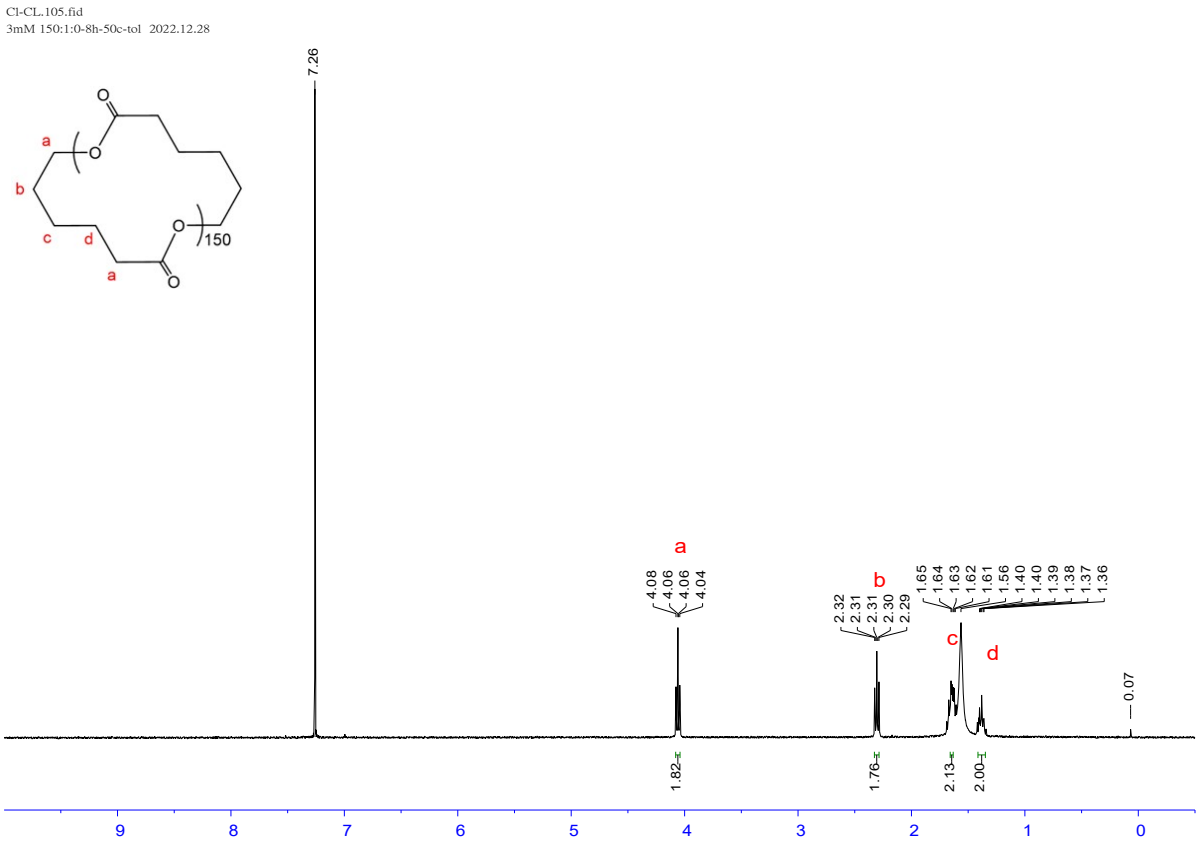



**Figure S8.** $^{1}$H NMR spectrum of PCL initiated by ε-CL/complex **1**/BnOH (150/1/0, Table 2, entry 14, $Mn_{(GPC)}$= 114.2 Kg/mol, $Đ$= 1.14)

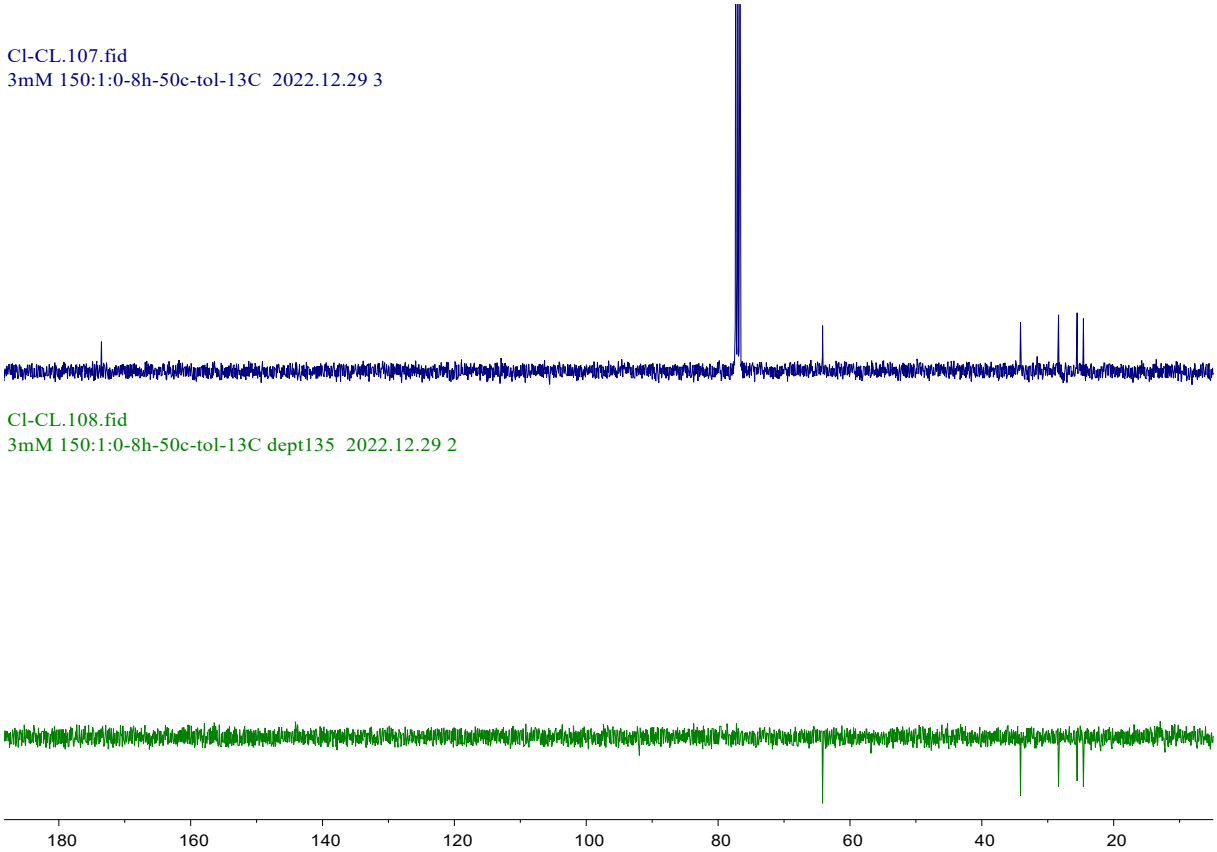
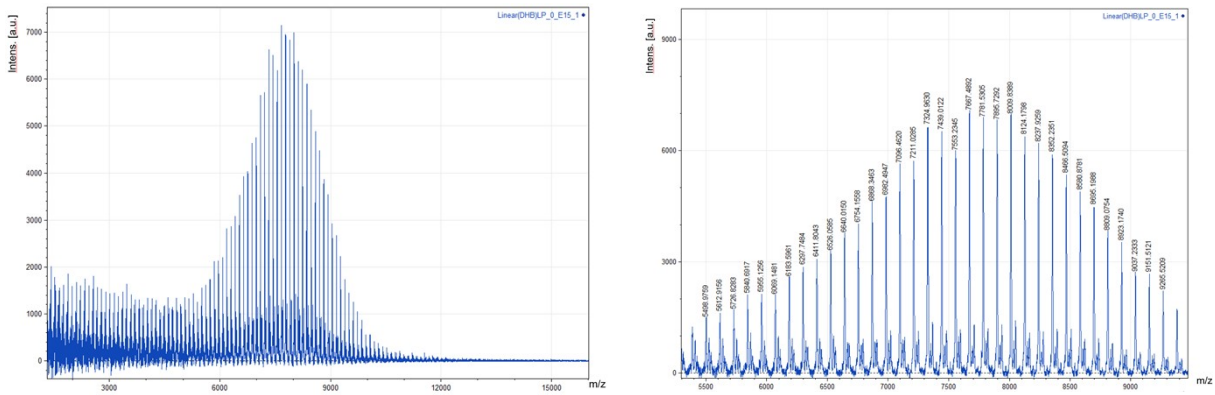



**Figure S9.** $^{13}$C NMR spectrum of PCL initiated by ε-CL/complex **1**/BnOH (150/1/0, Table 2, entry 14, $Mn_{(GPC)}$= 114.2 Kg/mol, $Đ$= 1.14)

(a) (b)




(c)

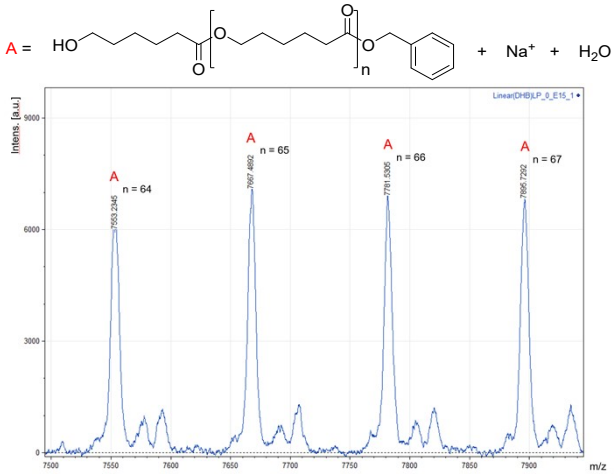
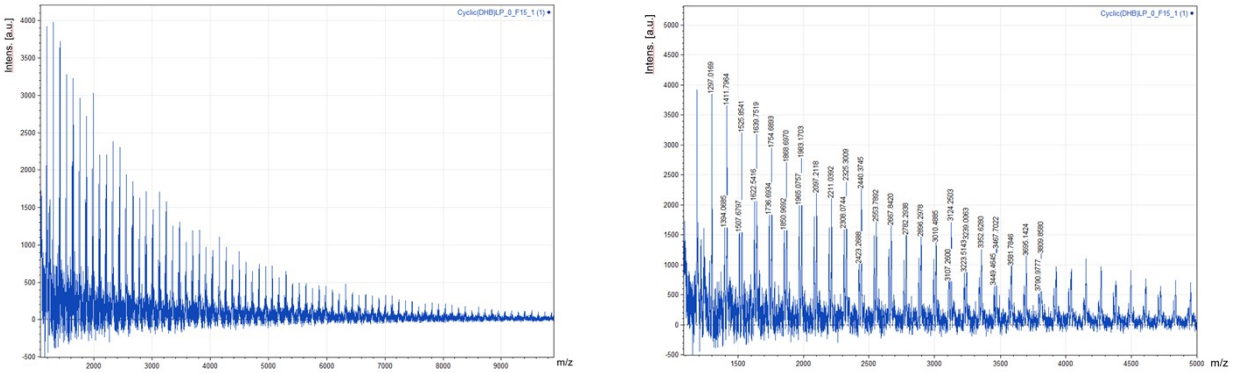
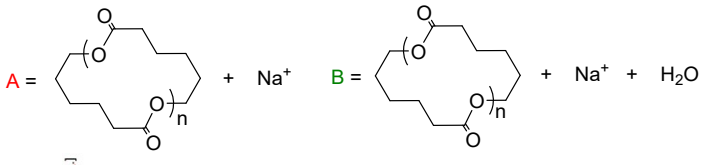



**Figure S10.** (**a**)-(**b**) MALDI-TOF spectrum of PCL initiated by ε-CL/complex **1**/BnOH (150/1/1, Table 2, entry 1, $Mn_{(GPC)}$= 23.2 Kg/mol, $Đ$= 1.12); (c) From m/z 7500 to 7900, PCL was analyzed by MALDI-TOF-MS.

(a) (b)




(c)



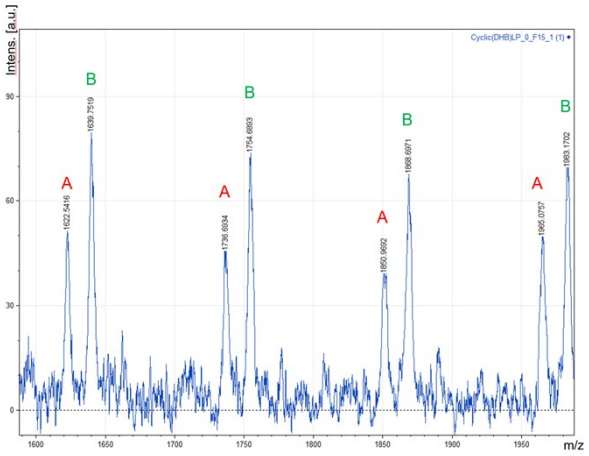




**Figure S11.** (**a**)-(**b**) MALDI-TOF spectrum of PCL initiated by ε-CL/complex **1**/BnOH (150/1/0, Table 2, entry 14, $Mn_{(GPC)}$= 114.2 Kg/mol, $Đ$= 1.14); (c) From m/z 1600 to 1950, PCL was analyzed by MALDI-TOF-MS.