**Substituent effect on the catalytic activity of dinuclear Zn(II) and Cu(II), 3- and 4-pyridinyl Schiff complexes in the ring-opening polymerization of cyclic esters**

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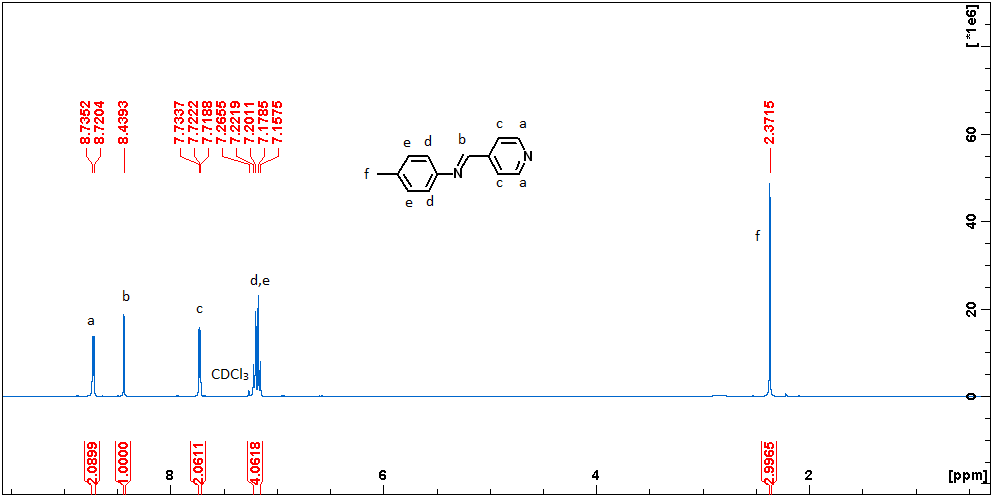
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# 1H NMR SPECTRA OF L1 – L10



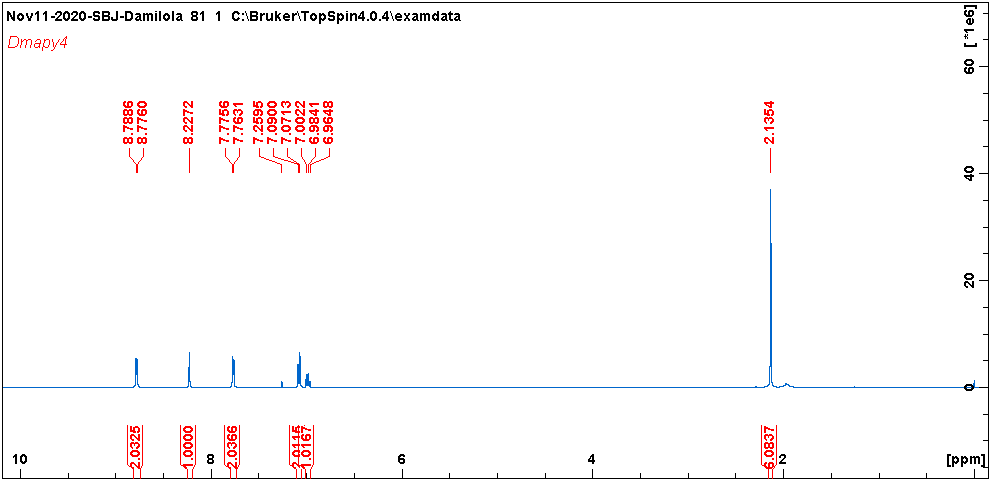
## Figure S1: (E)-N-(p-tolyl)-1-(pyridin-4-yl)methanimine L1

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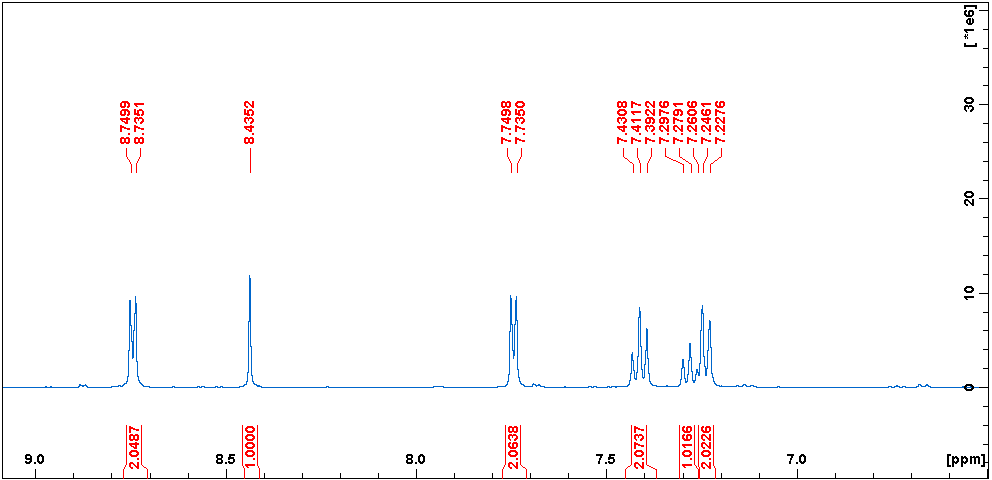
## Figure S2: (E)-N-(2,6-diisopropylphenyl)-1-(pyridin-4-yl)methanimine L2

C:\Users\Administrator\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ClPy4 1H.TIFF

## Figure S3: (E)-N-(4-chlorophenyl)-1-(pyridin-4-yl)methanimine L3



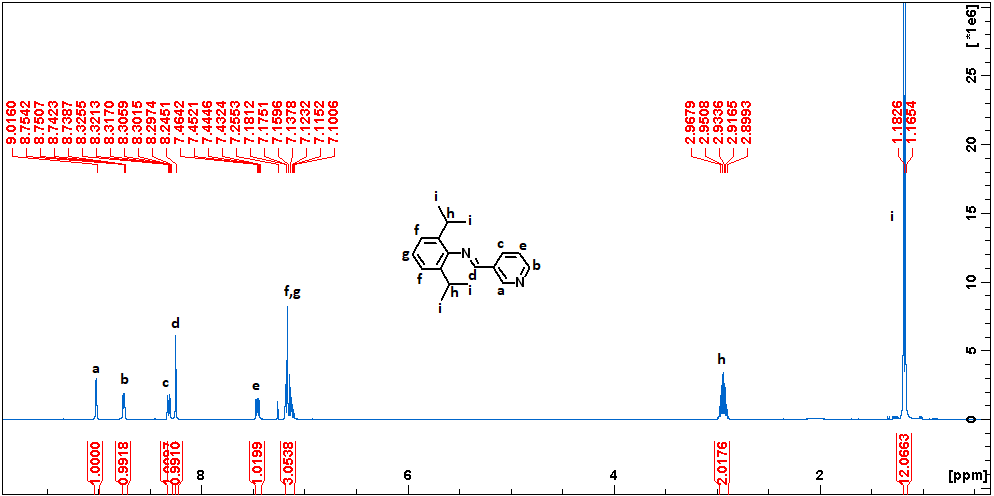
## Figure S4: (E)-N-(2,6-dimethylphenyl)-1-(pyridin-4-yl)methanimine L4



## Figure S5: (E)-N-phenyl-1-(pyridin-4-yl)methanimine L5

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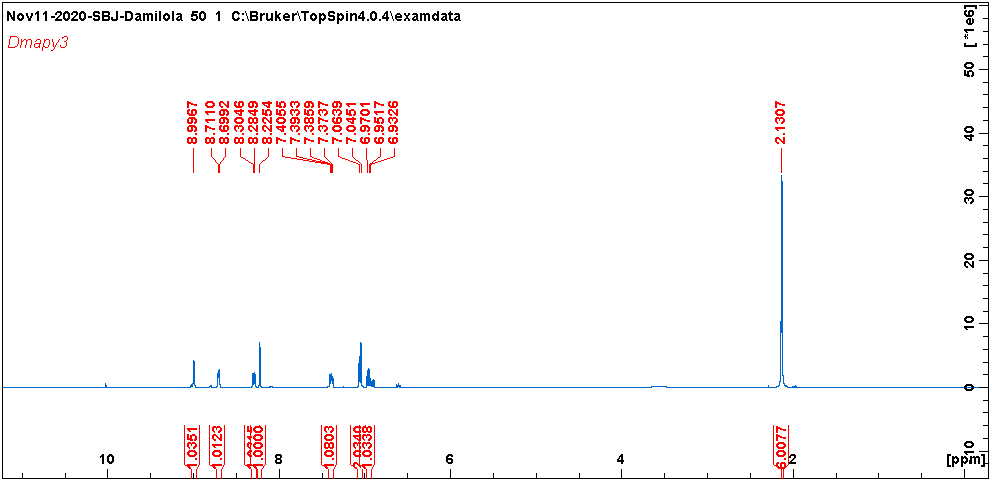
## Figure S6: (E)-1-(pyridin-3-yl)-N-(p-tolyl)methanimine L6



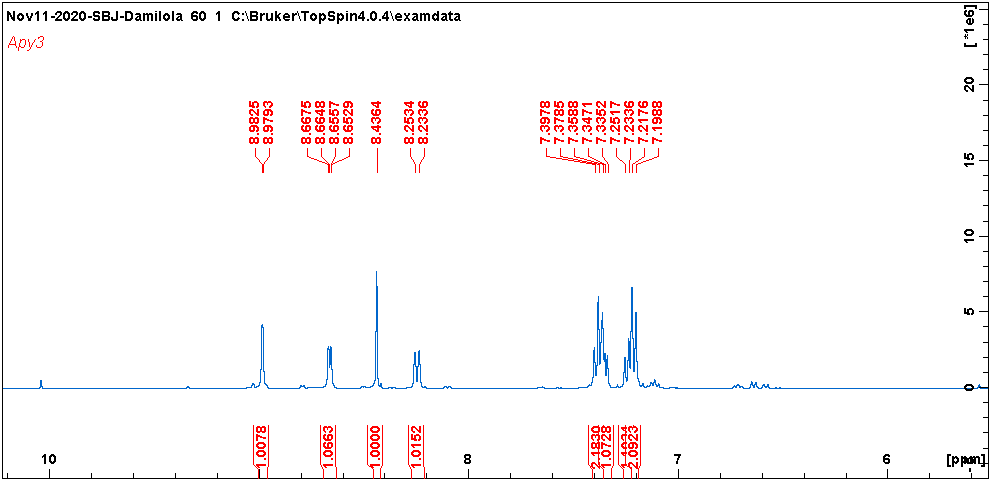
## Figure S7: (E)-N-(2,6-diisopropylphenyl)-1-(pyridin-3-yl)methanimine L7

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## Figure S8: (E)-N-(4-chlorophenyl)-1-(pyridin-3-yl)methanimine L8



## Figure S9: (E)-N-(2,6-dimethylphenyl)-1-(pyridin-3-yl)methanimine L9

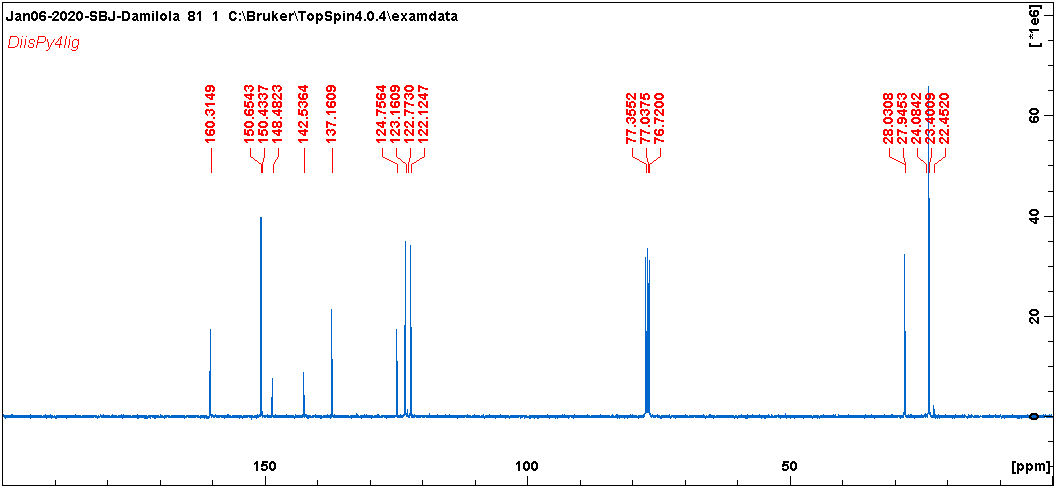


## Figure S10: (E)-N-phenyl-1-(pyridin-3-yl)methanimine L10

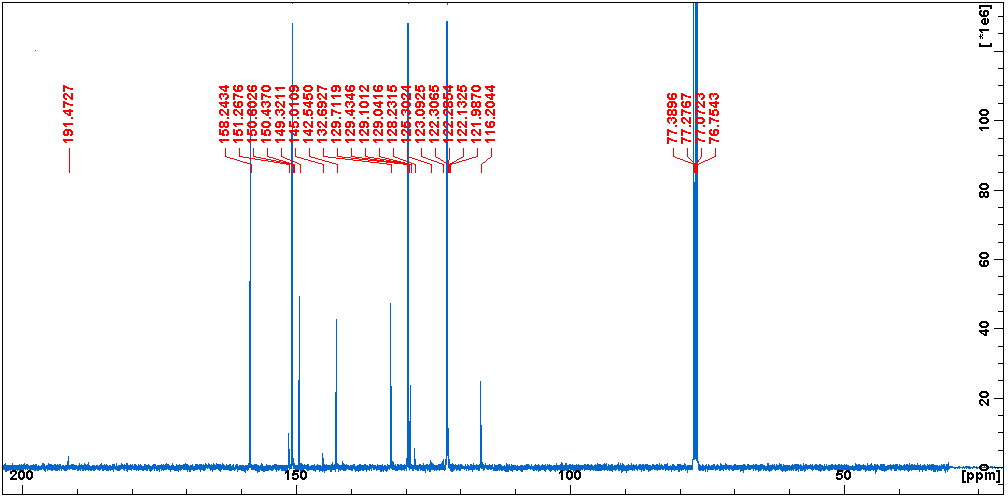
# 13C NMR spectra of L1 – L10

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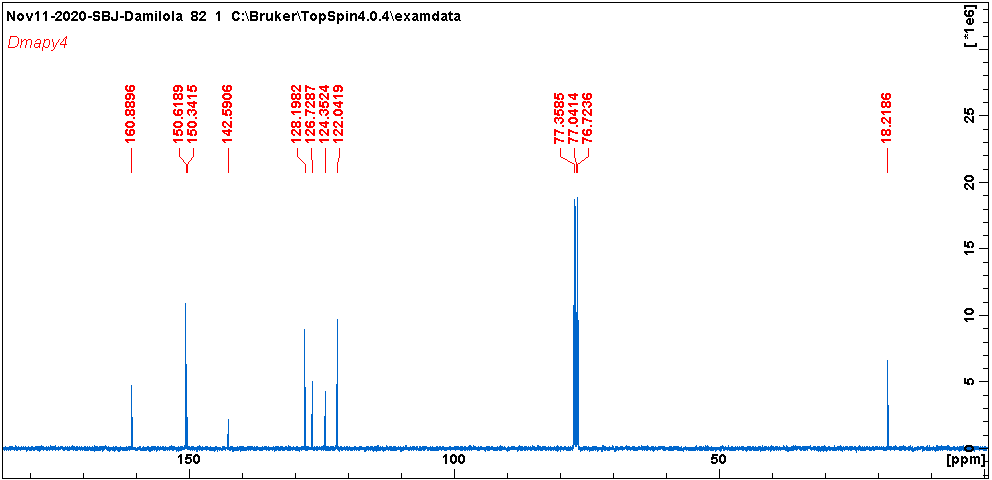
## Figure S11: (E)-N-(p-tolyl)-1-(pyridin-4-yl)methanimine L1



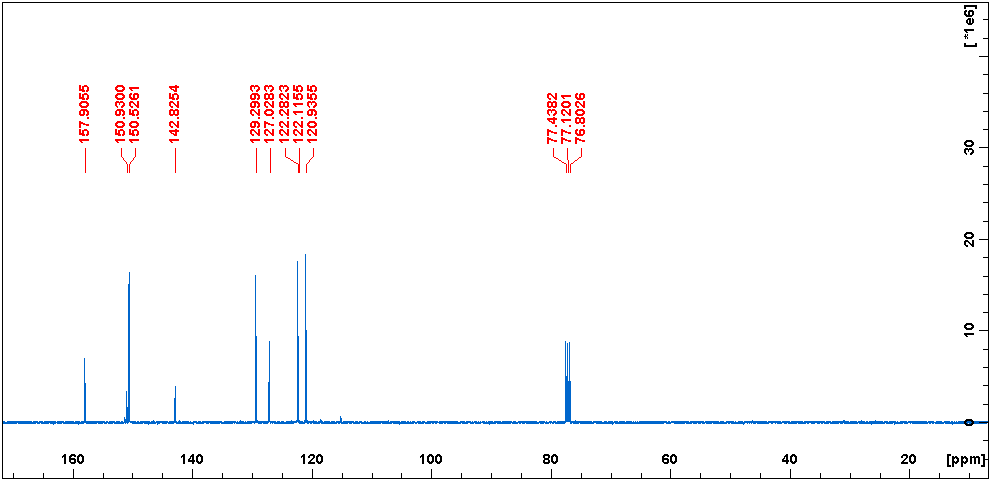
## Figure S12: (E)-N-(2,6-diisopropylphenyl)-1-(pyridin-4-yl)methanimine L2



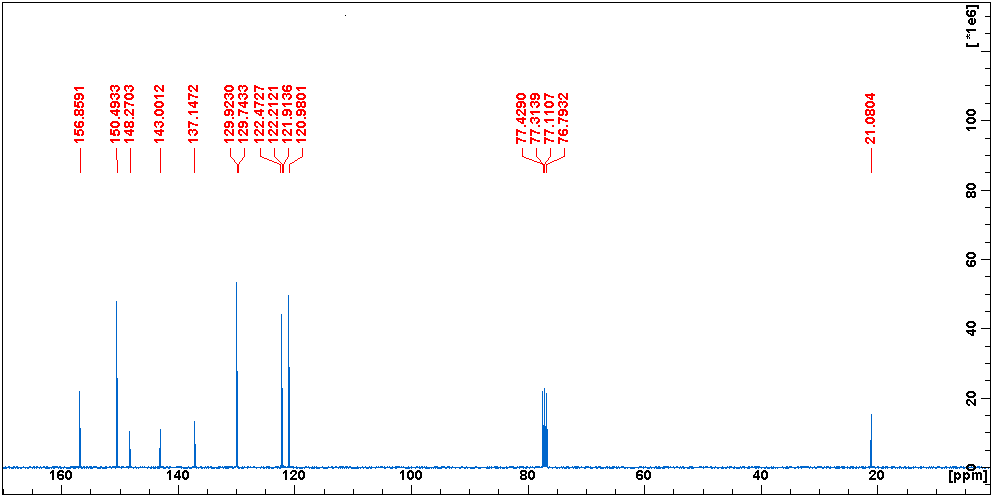
## Figure S13: (E)-N-(4-chlorophenyl)-1-(pyridin-4-yl)methanimine L3



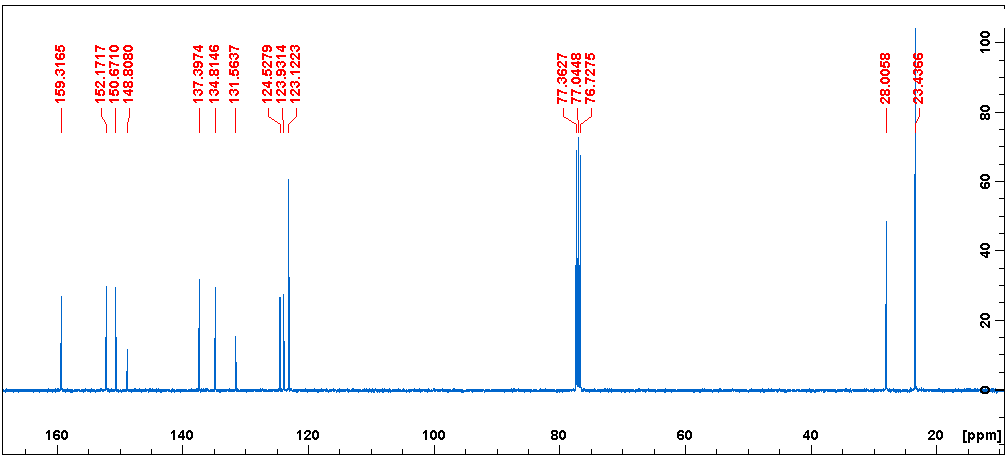
## Figure S14: (E)-N-(2,6-dimethylphenyl)-1-(pyridin-4-yl)methanimine L4



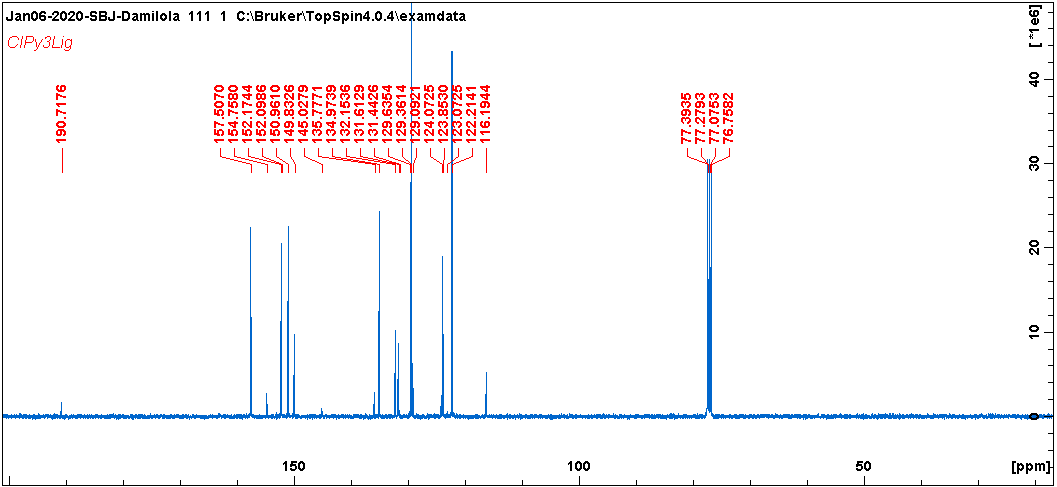
## Figure S15: (E)-N-phenyl-1-(pyridin-4-yl)methanimine L5



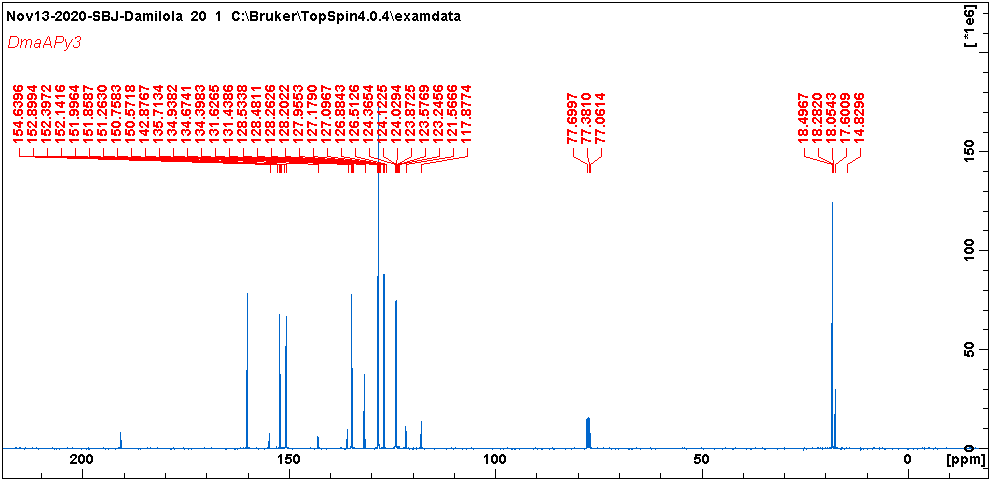
## Figure S16: (E)-1-(pyridin-3-yl)-N-(p-tolyl)methanimine L6



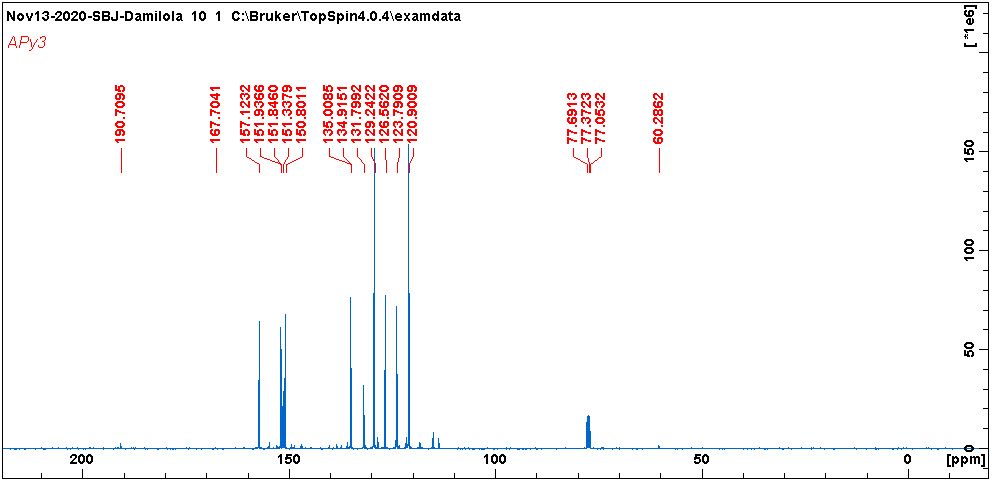
## Figure S17: (E)-N-(2,6-diisopropylphenyl)-1-(pyridin-3-yl)methanimine L7



## Figure S18: (E)-N-(4-chlorophenyl)-1-(pyridin-3-yl)methanimine L8



## Figure S19: (E)-N-(2,6-dimethylphenyl)-1-(pyridin-3-yl)methanimine L9



## Figure S20: (E)-N-phenyl-1-(pyridin-3-yl)methanimine L10

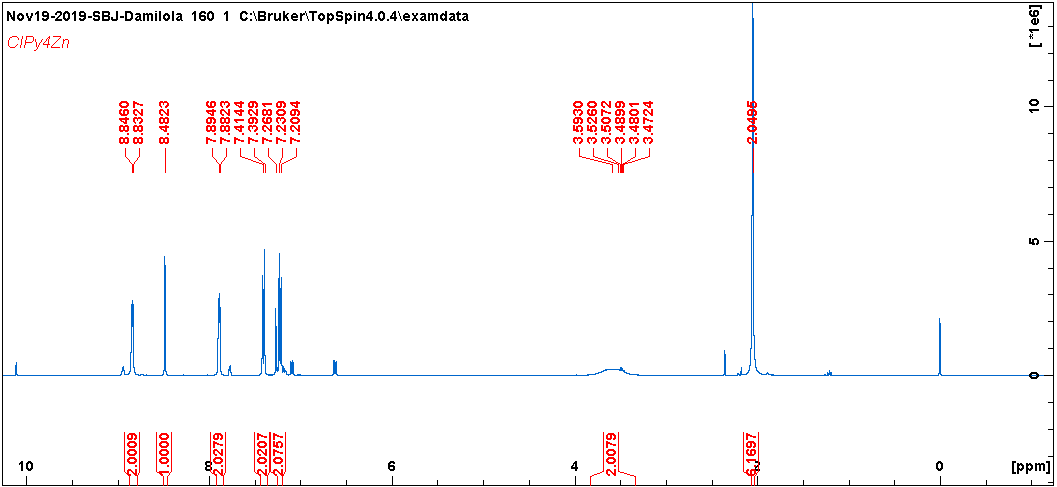
# 1H NMR spectra of complexes 1, 3 and 5



## Figure S21: 1H NMR spectrum of complex 1 in CDCl3 at room temperature

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## Figure S22: 1H NMR spectrum of complex 3 in CDCl3 at room temperature

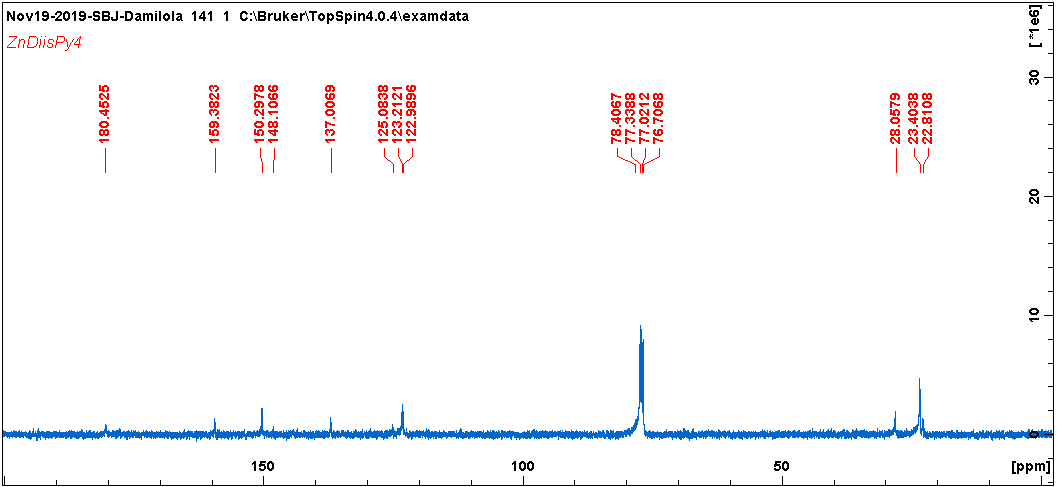


## Figure S23: 1H NMR spectrum of complex 5 in CDCl3 at room temperature

# 13C NMR spectra of complexes 1, 3 and 5



## Figure S24: 13C NMR spectrum of complex 1 in CDCl3 at room temperature.



## Figure S25: 13C NMR spectrum of complex 3 in CDCl3 at room temperature.

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## Figure S26: 13C NMR spectrum of complex 5 in CDCl3 at room temperature.

**Table S1**: Summarized wavelengths and transitions of complexes **1** – **13**

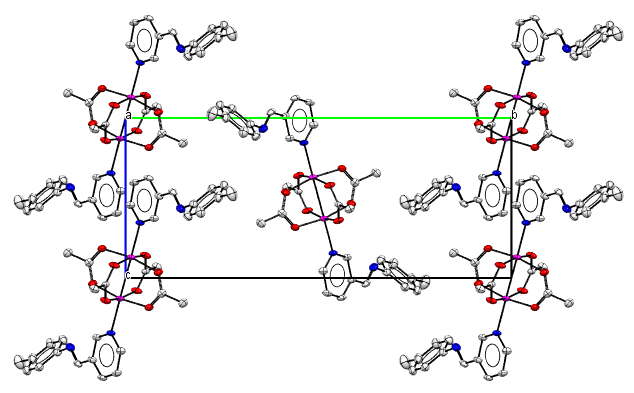
|  |  |  |
| --- | --- | --- |
| Complex | Wavelength | Transition |
| 1 | 241, 270, 332 | π-π\*, n-π\* |
| 2 | 234, 266, 334 | π-π\*, n-π\* |
| 3 | 241, 357 | π-π\*, n-π\* |
| 4 | 236, 346 | π-π\*, n-π\* |
| 5 | 241, 267, 330 | π-π\*, n-π\* |
| 6 | 234, 262, 325 | π-π\*, n-π\* |
| 7 | 234, 341 | π-π\*, n-π\* |
| 8 | 231, 260, 324 | π-π\*, n-π\* |
| 9 | 241, 325 | π-π\*, n-π\* |
| 10 | 246, 346 | π-π\*, n-π\* |
| 11 | 250, 325 | π-π\* π-π\*, |
| 12 | 241, 343 | π-π\*, n-π\* |
| 13 | 253, 325 | π-π\*, n-π\* |

**Table S2**: Shift in the proton of ligands and complexes

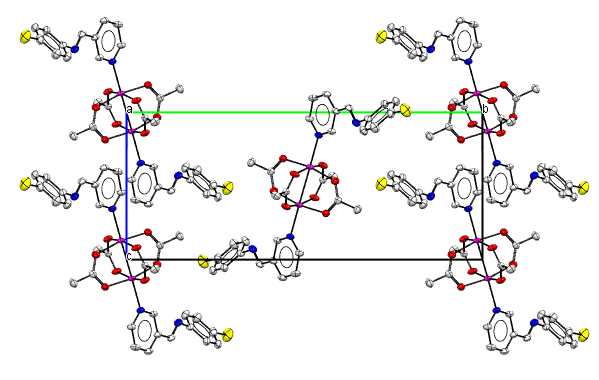
|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Complexes** | **NMR** | | | | | |
|  |  | d, py 2H | | Δυ | d, py 2H | | Δυ |
| Ligand | Complex | Ligand | Complex |
| 1 | **1** | 8.73 | 8.84 | 0.11 | 7.73 | 7.90 | 0.17 |
| 2 | **3** | 8.78 | 8.88 | 0.10 | 7.77 | 7.92 | 0.15 |
| 3 | **5** | 8.80 | 8.84 | 0.04 | 7.79 | 7.89 | 0.10 |



## Figure S27: An overlay of complex 9 (blue) and complex 11 (red)



## Figure S28: Packing diagram of complexes 9 as viewed down the crystallographic a-axis direction. Hydrogen atoms have been omitted for clarity.

****

## Figure S29: Packing diagram of complexes 11 as viewed down the crystallographic a-axis direction. Hydrogen atoms have been omitted for clarity.

## Figure S30: Pseudo-first-order logarithmic plot for the polymerization of *rac*-LA and L-LA in toluene at 110 °C by complex 5.

## Figure S31: Pseudo-first-order logarithmic plot for the bulk polymerization of CL at 110 °C by complexes 2, 4, 6, 7 and 8.

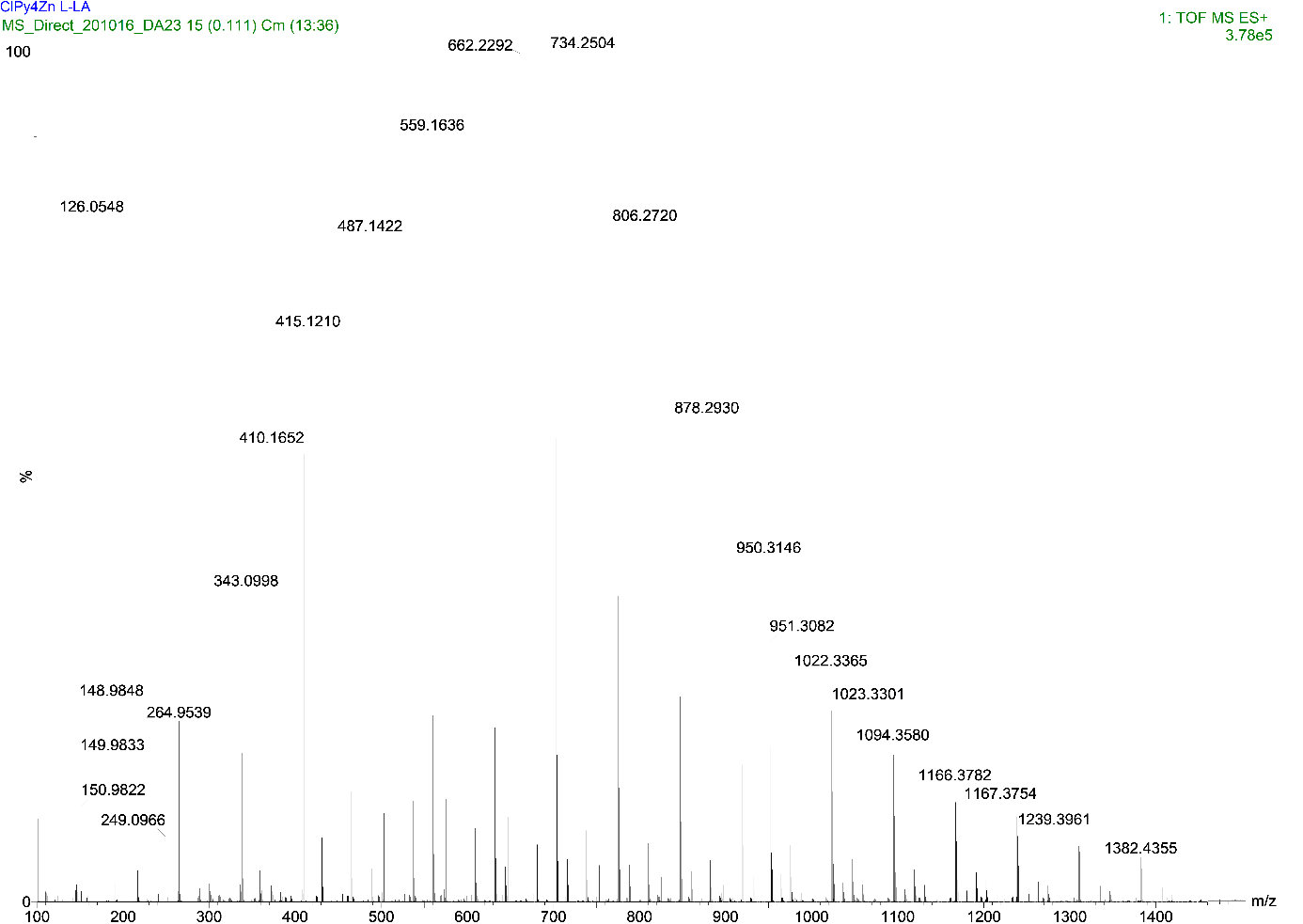
## Figure S32: Pseudo-first-order logarithmic plot for the bulk polymerization of CL at 110 °C by complexes 9, 10, 11, 12 and 13.

**complete alcohol study 1H NMR**

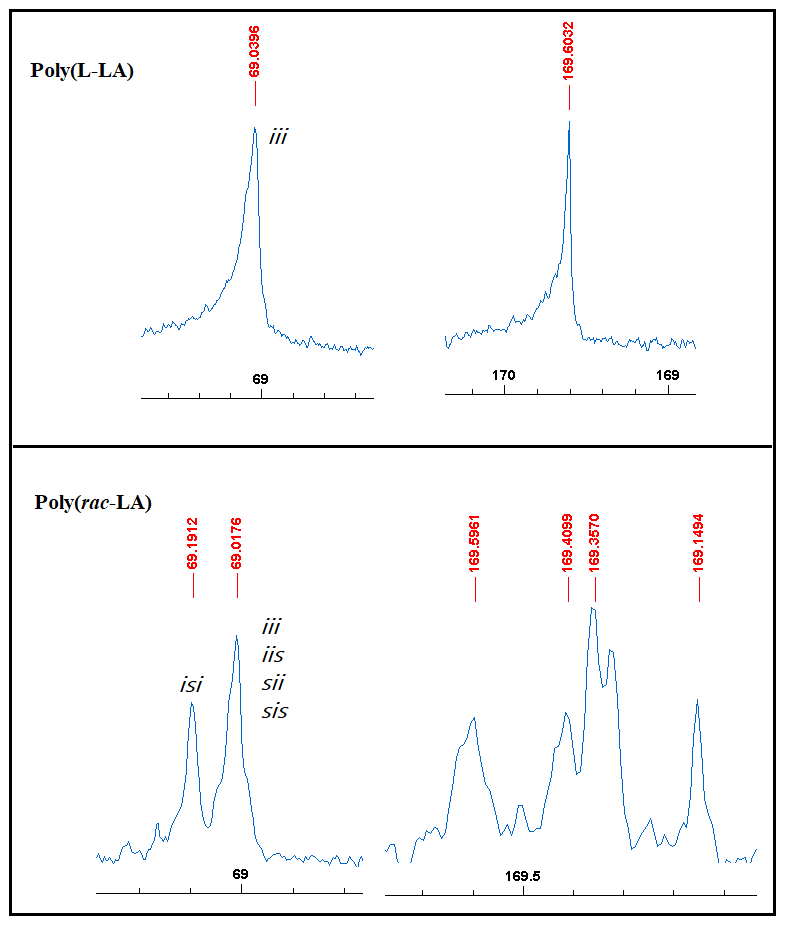
## Figure S33: The 1H-NMR spectrum of poly(ε-CL) initiated by complex 7 in different alcohol at room temperature in CDCl3 (400 MHz). Reaction conditions: [CL] 0 :[I]0:[ROH]0 = 200:1, bulk, T = 110 °C

Full spectrum for LA by ClPy4Zn

## Figure S34: The 1H-NMR spectrum of poly(L-LA) initiated by complex 5 at room temperature in CDCl3 (400 MHz). Reaction conditions: [LA] 0 :[I]0 = 200:1, bulk, T = 110 °C.

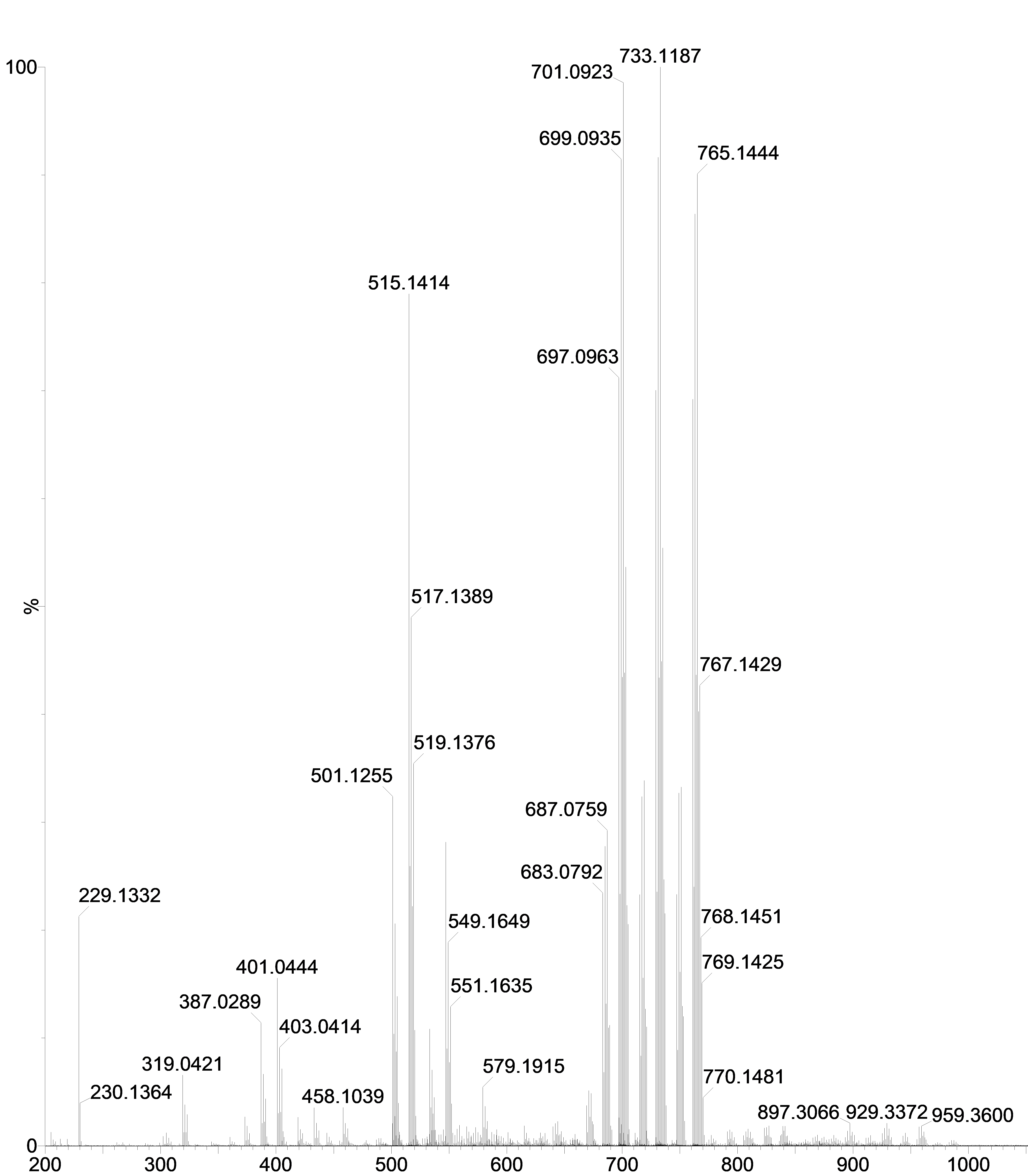
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## Figure S35: ESI-MS spectrum of poly(L-LA) initiated by complex 5. Reaction conditions: [LA]0 :[I]0 = 200:1, bulk, T = 110 °C.

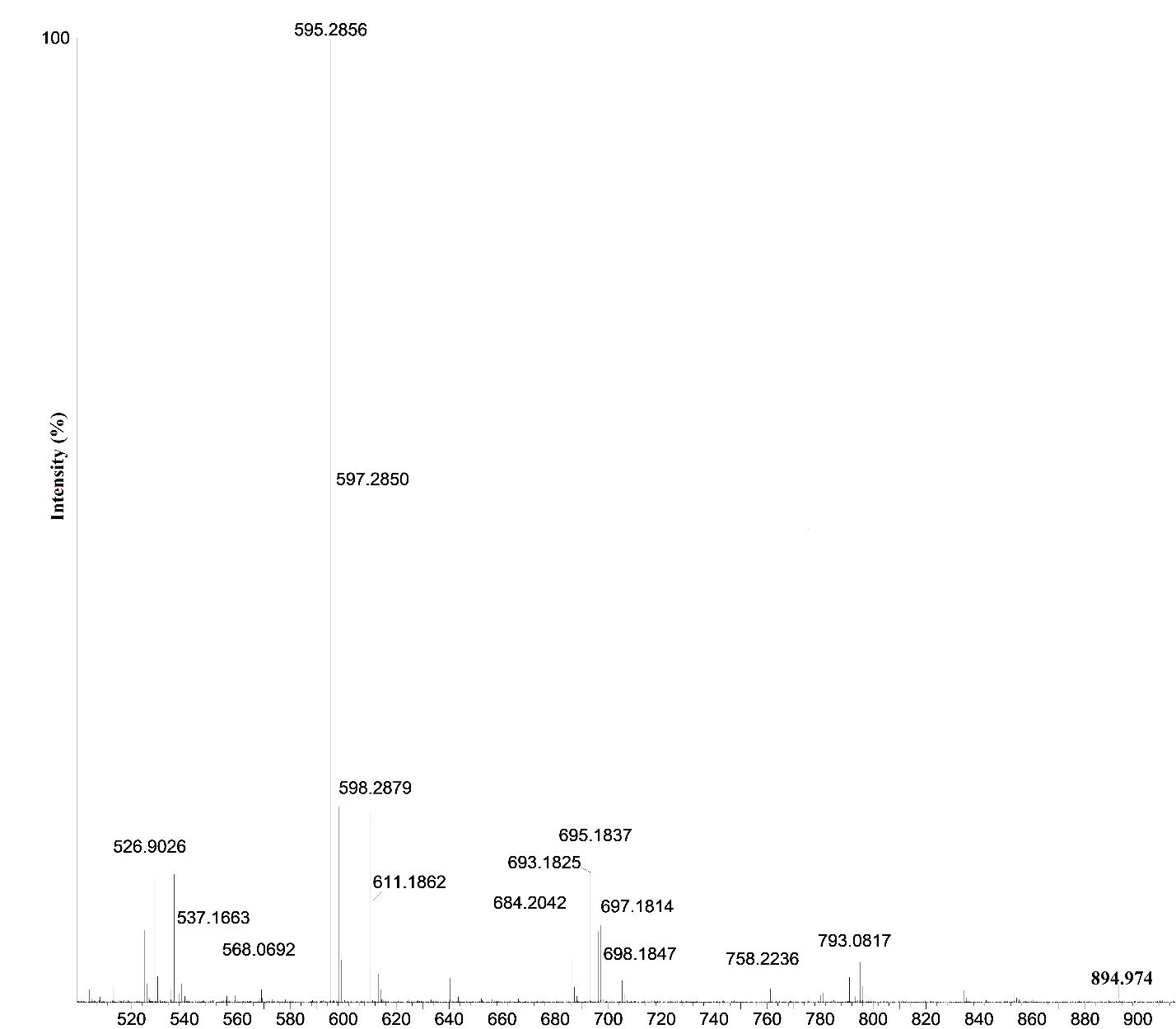


## Figure S36: 13C NMR spectrum of the methine and carbonyl region of PLA obtained by complex 5 in CDCl3 at room temperature.

# MASS SPECTRA OF CARBOXYLATE COMPLEXES



## Figure S37: ESI-MS spectrum of complex 1



## Figure S38: ESI-MS spectrum of complex 10

# MASS SPECTRA OF POLYMERS



## Figure S39: ESI-MS spectrum of PCL obtained from complex 7



## Figure S40: ESI-MS spectrum of PCL obtained from complex 7 in benzyl alcohol



## Figure S41: ESI-MS spectrum of PCL obtained from complex 7 in isopropyl alcohol



## Figure S42: ESI-MS spectrum of poly(*rac*-lA) obtained from complex 5